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NOTICE

The eighteenth Scientific Meeting of the Academy will be held on Saturday, 7th August 1937, at 5-15 p.m., in the Central Building of the Indian Institute of Science, Bangalore.

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ON A METHOD OF SOLVING LINEAR DIFFERENTIAL EQUATIONS IN SERIES.

By S. L. Malurkar,
Agra.

Received December 1, 1936.

Given a linear differential equation

$$f(\mathrm{D})\,y + \mathrm{I}y = 0$$

where $\mathrm{D} = d/dx$; and I is a function of x only, it is a common method of solution to substitute for y in the above equation a series of form $\Sigma\, a_n\, u_n\,(x)$ where the a's are constants and u's are linearly independent functions of x only and obtain the values of the constant coefficients. There occur several problems in applied mathematics where the above method is insufficient to determine the mutual relation between the coefficients. Also the usually known methods of solving the differential equations do not lead to solutions which would be readily interpretable for the actual problems. As a particular example one may notice

$$(\mathrm{D}^2 - a^2)^m\, y = \mathrm{I}y$$

which type of equations occur in stability problems. As the method is capable of application to other problems also, a brief account of the method of solution that has been introduced would perhaps be of interest.*

Take the very simple example

$$\mathrm{D}^2 y - p^2 y = 0$$

and assume, in the interval $-\pi < x < \pi$, a fourier series $\frac{1}{2}\mathrm{A}_0 + \Sigma\,\mathrm{A}_n \cos nx + \Sigma\,\mathrm{B}_n \sin nx$ and substitute this in the differential equation and equate the coefficients of $\cos nx$ and $\sin nx$ to zero. The only relation that is obtained is $\mathrm{A}_0 = 0 = \mathrm{A}_n = \mathrm{B}_n$ unless ip is a real integer. This null solution is obviously incorrect as it is well known that $\cosh px$ and $\sinh px$ have valid fourier expansions in the interval. However in this particular example, the solution could have been obtained otherwise.

Returning to the general problem let $f(\mathrm{D})$ be a polynomial in D and let it be assumed that the differential equation $f(\mathrm{D})\,y = 0$ can be completely

* See *e.g.* "On the Differential Equation of the Instability Problems." S. L. Malurkar and M. P. Srivastava. *Proc. Ind. Acad. Sci.*, 1937, **5**, 34.

solved in terms of known functions. With the knowledge of this solution the complete solution of the equation

$$f(\mathrm{D})\, y = \mathrm{I}y \tag{1}$$

is attempted here.

Assume that in the interval $-\pi < x < \pi$

$$y = \tfrac{1}{2}\mathrm{A}_0 + \Sigma\, \mathrm{A}_n \cos nx + \Sigma\, \mathrm{B}_n \sin nx$$

Substitute this value of y only on the right side of the equation in (1). Then it can be written as

$$f(\mathrm{D})\, y = \{\tfrac{1}{2}\mathrm{A}_0 + \Sigma\, \mathrm{A}_n \cos nx + \Sigma\, \mathrm{B}_n \sin nx\}\, \mathrm{I} \tag{2}$$

The solution of equation (2) is

$$y = \mathrm{Y} + \mathrm{P}(x)$$

where Y is the complementary solution involving the appropriate number of arbitrary constants and $\mathrm{P}(x)$ is a particular solution of the modified differential equation (2). Let it be assumed that Y and $\mathrm{P}(x)$ can be developed as fourier series. Let $\mathrm{P}(x)$ be written as

$$\tfrac{1}{2}\mathrm{C}_0 + \Sigma\, \mathrm{C}_n \cos nx + \Sigma\, \mathrm{D}_n \sin nx$$

The C's and D's are obviously functions of the A's and B's. Comparing the fourier series for $\mathrm{Y} + \mathrm{P}(x)$ with the original assumption for y, it easily follows that

$$\begin{aligned}
\mathrm{A}_0 - \mathrm{C}_0 &= \frac{1}{\pi} \int_{-\pi}^{\pi} \mathrm{Y} dx \\
\mathrm{A}_n - \mathrm{C}_n &= \frac{1}{\pi} \int_{-\pi}^{\pi} \mathrm{Y} \cos nx\, dx \\
\mathrm{B}_n - \mathrm{D}_n &= \frac{1}{\pi} \int_{-\pi}^{\pi} \mathrm{Y} \sin nx\, dx
\end{aligned} \tag{3}$$

Hence the C's and D's and therefore the A's and B's are obtained as functions of the arbitrary constants involved in Y. The function $\mathrm{P}(x)$ can be expressed free from unknown constants apart from those involved in Y. The arbitrary constants can be evaluated by applying the boundary conditions to the function $\mathrm{Y} + \mathrm{P}(x)$. Then the values of the A's and B's are determinable completely.

In this method it may be pointed out that the equation (1) is solved in two stages. An assumption for y in a series form is made only for a portion of the terms of the differential equation. Then the modified differential equation is solved completely. The solution now obtained is compared or equated to the original assumption.

A simple example of the application of the method to a differential equation whose solution can also be found out by other simpler methods is given here. Take

$$d^2y/dx^2 - a^2y = \lambda^2 y \tag{4}$$

In the interval $0 < x < \pi$ it is sufficient to assume a fourier sine series in the form

$$y = \Sigma\, A_n \sin nx$$

Then the equation (4) is transformed to

$$d^2y/dx^2 - a^2y = \lambda^2\, \Sigma\, A_n \sin nx \tag{5}$$

and this modified equation is solved.

It is easy to show that the solution of (5) is

$$y = B \cosh a\,(\pi/2 - x) + C \sinh a\,(\pi/2 - x)$$
$$- \lambda^2\, \Sigma\, A_n \sin nx/(n^2 + a^2)$$

The forms $\cosh a\,(\pi/2 - x)$ and $\sinh a\,(\pi/2 - x)$ are better as the fourier expansions of these need contain either only the odd or even multiples of x. As in the interval $0 < x < \pi$

$$\cosh a\,(\pi/2 - x) = \frac{2}{\pi} \sum_1^\infty n\,(1 - \cos n\pi) \cosh a\pi/2 \sin nx/(n^2 + a^2)$$

and

$$\sinh a\,(\pi/2 - x) = \frac{2}{\pi} \sum_1^\infty n\,(1 + \cos n\pi) \sinh a\pi/2 \sin nx/(n^2 + a^2)$$

it follows from a comparison of the solution of the (5) with the assumed series for y before the modification was made that

$$A_n = \frac{2B \cosh a\pi/2}{\pi(n^2 + a^2)}\,(1 - \cos n\pi) + \frac{2C \sinh a\pi/2}{\pi(n^2 + a^2)}\,(1 + \cos n\pi)$$
$$- \lambda^2 A_n/(n^2 + a^2)$$

or

$$A_n = \frac{2n}{\pi(n^2 + a^2 + \lambda^2)} \{B \cosh a\pi/2\,(1 - \cos n\pi) + C \sinh a\pi/2\,(1 + \cos n\pi)\}$$

Hence comparing with the expansions above it is seen that

$$y = \frac{B \cosh a\pi/2}{\cosh b\pi/2} \cosh b(\pi/2 - x) + \frac{c \sinh a\pi/2}{\sinh b\pi/2} \sinh b(\pi/2 - x)$$

where $b^2 = a^2 + \lambda^2$ which would have been the solution had the differential equation been solved in the form

$$(d^2/dx^2 - b^2)\, y = 0$$

Take another example

$$d^2y/dx^2 + p^2y = 0 \tag{6}$$

where p is not an integer and the solution which vanishes at $x = 0$ and $x = \pi$ is required. The equation might be split up into two portions as

$$d^2y/dx^2 = -p^2y$$

Assume that in the interval $0 < x < \pi$ y has the expansion $\Sigma\ A_n \sin nx$. The modified differential equation which has to be solved is

$$d^2y/dx^2 = -p^2\ \Sigma\ A_n \sin nx$$

whose solution is obviously

$$L + Mx - p^2\ \Sigma\ \frac{A_n}{n^2}\ \sin nx$$

Comparing this with the original assumption it follows that

$$2\ (1 - \cos n\pi)\ L - 2M \cos n\pi = \pi n\ A_n\ (1 - p^2/n^2)$$

Applying the boundary conditions to the form of the solution obtained after integration it follows that

$$L = 0 = M = A_n \text{ and hence } y = 0$$

In any practicable method of solution of any differential equation in series, term by term differentiation enters invariably and the justification of the process can be made mostly after the solution has been obtained in some series form. If the resulting series lead to divergent types the process is given up as not legitimate. In the present method, *i.e.*, in the determination of the particular solution of the modified differential equation term by term integration is mostly involved. The necessary justification of convergence of the solution obtained will be less than in the case of term by term differentiation.

The method given above can be put slightly in a more general symbolic form. If the differential equation $f(D)\ y = 0$ can be split up into two terms and the equation is capable of being written as

$$f_1(D)\ y + f_2(D)\ y = 0 \tag{7}$$

where $f_1(D)$ and $f_2(D)$ are two polynomials in D and the order of the polynomial f_1 is greater than that of the polynomial f_2; it may be assumed that

$$y = \tfrac{1}{2}\ A_0 + \Sigma\ (A_n \cos nx + B_n \sin nx)$$

and the differential equation may be solved in the modified form

$$f_1(D)\ y = -f_2(D)\ \{\tfrac{1}{2}\ A_0 + \Sigma\ (A_n \cos nx + B_n \sin nx)\} \tag{8}$$

This equation may be solved as before with the knowledge of the solution of $f_1(D)\ y = 0$ in the form $y = Y + P(x)$. Comparing the fourier coefficients of $Y + P(x)$ with the A's and B's, the mutual relations are obtained. By applying the boundary conditions to $Y + P(x)$ as before the complete solution is obtained.

Instead of assuming fourier type of series, it is often possible and sometimes preferable to assume expansions involving other functions which form a complete orthogonal set, *e.g.*, the Legendre functions, the normal Mathieu functions or the many wave-functions that have come into prominence in quantum mechanics. Of course in these cases f (D) need not be purely a polynomial in D. The differential equation is broken up into two suitable parts in one of which the series in terms of the orthogonal functions is substituted. The modified differential equation is then completely solved and this solution is compared with the original assumed expansion and the coefficients determined.

In subsequent papers the author hopes to publish the utility of these methods in solving actual problems in applied mathematics.

HETEROCYCLIC COMPOUNDS.

Part III. The Synthesis of Cyclopenteno-(1': 2': 2 : 3)-chromones, and a Discussion on the Mechanism of the Pechmann and the Simonis Reactions.

By S. Zafaruddin Ahmad and R. D. Desai.

(*From the Department of Chemistry, Muslim University, Aligarh.*)

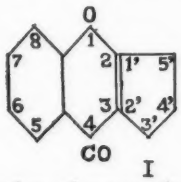
Received May 10, 1937.

(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

The condensation of phenols with open-chain β-ketonic esters in the presence of concentrated sulphuric acid, usually known as the Pechmann Reaction[1] has been a prolific source of the synthesis of substituted coumarins or 1 : 2-benzopyrones. Later on, Simonis[2] showed that this reaction could be made to give chromones or 1 : 4-benzopyrones by substituting phosphorus pentoxide for concentrated sulphuric acid. Jacobson and Ghosh,[3] on the other hand, reported the formation of chromones in the Pechmann Reaction, when one of the hydrogens of the reactive methylene group of the β-ketonic ester was replaced by a sufficiently bulky group. Unfortunately, all the alleged chromones were proved to be coumarins by Baker and Robinson,[4] and, therefore, there existed considerable doubt if chromones could at all be produced by the Pechmann Condensation. However, the isolation of a chromone in the condensation of acetoacetic ester with β-naphthol in the presence of concentrated sulphuric acid by Dey and Lakshminarayanan[5] has shown the existence of this possibility, though it must be admitted that this is the only observation of its kind.

The Simonis Reaction itself has been the subject of an exhaustive and critical investigation independently by Robertson[6] *et al.* as well as D. Chakravarti[7] and his co-workers. Robertson came to the conclusion which he recanted afterwards that the chromone formation depended mainly on the character of the phenol. Chakravarti is of opinion that the formation of the chromone is governed by the nature of the phenols as well as the β-ketonic esters. Only those phenols which do not undergo the Pechmann Reaction or do it reluctantly give chromones. With regard to the β-ketonic esters, alkyl groups in the α-position favour chromone formation. Phosphorus pentoxide is the only condensing agent which promotes the chromone formation when other favourable conditions are present, the only exception being the case noted by Dey and Lakshminarayanan (*loc. cit.*).

As literature showed the absence of work on the formation of chromones from phenols and cyclic β-ketonic esters, we took up this investigation to see how these esters compare themselves with their open-chain analogues with regard to the Simonis Reaction. We have been able to prepare chromones from phenol, *m*-cresol, *p*-cresol and β-naphthol by condensing them with ethyl-cyclopentanone-2-carboxylate in the presence of phosphorus pentoxide. Phosphorus oxychloride which has been recently recommended by Robertson *et al.* (*loc. cit*) for this purpose is not as convenient as phosphorus pentoxide because of the formation of tarry and coloured by-products. Following the nomenclature[8] of the coumarins, we have named the chromone from ethyl cyclopentanone-2-carboxylate and phenol as cyclo-penteno-(1' : 2' : 2 : 3)-chromone or cyclopenteno-(1' : 2' : 2 : 3)-1 : 4 benzo-pyrone (I). These chromones condense with aldehydes with the formation of styryl derivatives as noticed by Chakravarti, Heilbron and others,[9] and are soluble in HCl (I : I). Their melting points and mixed melting points with the isomeric coumarins described by the authors in Part I of this series leave no ambiguity regarding their structure which is finally confirmed by their alkaline hydrolysis into ketones and *o*-hydroxy-acids (II). These chromones thus offer a marked contrast to the isomeric coumarins which are stable to alkaline hydrolysis, and simulate the behaviour of tetrahydro-xanthone synthetically prepared by M. Sen.[10]



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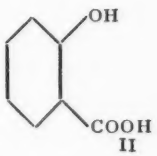


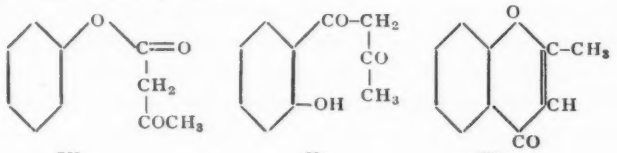
II

The formation of coumarins in the Pechmann Reaction has always been cited as a proof of the enolic nature of β-ketonic esters. The effect of substituents in the α-position of the β-ketonic esters will be to enhance or retard the enolisation, and experimental evidence bears out that substituents like halogens which tend to increase the tendency for enolisation give better yields of coumarins, while the opposite effect is observed in the case of alkyl groups which will suppress enolisation. This explanation is quite plausible so far as the part played by the ester is concerned, but it does not take count of the rôle played by the phenol. The alternative explanation which is worthy of consideration is, that the reactive hydrogen of the phenols which undergo the Pechmann Reaction co-ordinates itself readily with the carbonyl group of the ketonic ester. This hydrogen must always be in the *ortho*-position to the phenolic hydroxyl group and should

be sufficiently reactive, otherwise the tendency for the formation of the additive product will be either small or nil. The additive product (III) which is thus first formed, undergoes dehydration and cyclisation to coumarins. Any dehydrating agent can function as a condensing agent, and this is the reason why many condensing agents have been found serviceable in the Pechmann Reaction, though they differ among themselves with regard to their efficiency. The substituent in the β-ketonic ester will either facilitate or retard the formation of the additive product (III), and the effect will be partly polar and partly steric.

III

The mechanism of the Simonis Reaction is fundamentally different. By this reaction, we mean the interaction of phenols and β-ketonic esters in the presence of phosphorus pentoxide with the formation of chromones only. Chakravarti (*loc. cit.*) has already observed that those phenols which do not contain a reactive hydrogen *ortho* to the hydroxyl group give the chromones in this reaction. Therefore, it is plausible to assume that the reactive hydrogen in the case of the phenols which undergo the Simonis Reaction belongs to the hydroxyl group which interacts with the β-ketonic esters giving the aryl esters of these acids. These aryl esters undergo an isomeric change analogous to the Fries Transformation with the formation of *o*-hydroxy-benzoyl-acetylmethane (V) which is dehydrated to 2-methyl-chromone (VI). The specific condensing action of phosphorus pentoxide may be in facilitating the formation of either (IV) or (V) or both, as the conversion of (V) into (VI) may be accomplished with the help of any dehydrating agent. The intermediate formation of *o*-hydroxy-aroylacetyl-methanes in the Kostanecki Reaction has been proved by Baker,[11] and we are of opinion that this stage is also produced in the course of the Simonis Reaction. We have already some experimental work on hand to test the assumptions made, as well as to synthesise the chromones from other cyclic β-ketonic esters and phenols.



IV V VI

Experimental.

Cyclopenteno-(1' : 2' : 2 : 3)-*chromone.*—An intimate mixture of phenol (2 g.), ethylcyclopentanone-2-carboxylate (2 g.) and phosphorus pentoxide (5 g.) was heated in a round bottom flask on a water-bath for three hours. The cooled mass was treated with water and warmed up for some time, cooled, extracted with ether, and the ethereal extract washed twice with an excess of 5 per cent. caustic soda solution, dried, and the solvent recovered. The residue deposited crystalline needles on standing in a vacuum, and these were carefully washed with ether to remove the gummy impurities and finally crystallised from ether, when white needles (m.p. 120°) were obtained and the m.p. was depressed to 90° by admixture with the isomeric coumarin (m.p. 129°). (Found : C, 77·0 ; H, 5·4 ; $C_{12}H_{10}O_2$ requires C, 77·4 ; H, 5·4 per cent.)

The chromone is easily soluble in alcohol, acetic acid, acetone, benzene, ether, etc., but almost insoluble in petrol.

The *styryl derivative* was prepared by keeping overnight the alcoholic solution of the chromone (0·5 g.), benzaldehyde (0·5 g.) and sodium ethoxide (0·5 g. Na in 10 c.c. abs. alcohol). The solid was filtered off, and crystallised from alcohol in white needles (m.p. 161°). (Found : C, 83·1; H, 5·2; $C_{19}H_{14}O_2$ requires C, 83·2 ; H, 5·1 per cent.)

Alkaline hydrolysis.—The chromone (0·2 g.) was heated with N.NaOH (10 c.c.) for two hours on a sand-bath under reflux. After dilution with water, the alkaline solution was extracted with ether, and acidified with concentrated HCl. The acid obtained on cooling melted at 155°, and was identified as salicylic acid by comparison with an authentic specimen.

6-*Methylcyclopenteno*-(1' : 2' : 2 : 3)-*chromone.*—A mixture of *p*-cresol (3 g.), the ester (4 g.) and phosphorus pentoxide (6 g.) was heated on a water-bath for six hours and then at 130°–140° for one hour. The insoluble residue left after decomposing the mass with water was taken up in ether and the solution washed completely with alkali to remove the phenol, dried and the solvent recovered. On keeping in a vacuum the chromone solidified, and the solid then crystallised from ether in colourless needles (m.p. 144°). The isomeric coumarin melts at 174°. It resembled the parent substance in solubility and was hydrolysed by alkali to 2-hydroxy-5-methyl-benzoic acid[12] (m.p. 150°). (Found : C, 77·8 ; H, 6·1 ; $C_{13}H_{12}O_2$ requires C, 78·0 ; H, 6·0 per cent.)

7-*Methyl-cyclopenteno*-(1' : 2' : 2 : 3)-*chromone.*—An intimate mixture of the ester (3 g.), *m*-cresol (3 g.) and phosphorus pentoxide (6 g.) was heated on a water-bath for half an hour, and then at 130°–140° for another half an

hour. The mixture which charred and swelled appreciably was decomposed with water and the insoluble portion taken up in ether, washed with alkali-dried, and the solvent recovered. The residue which solidified after some time in a vacuum crystallised from ether-petrol (b.p. 40°–60°) mixture in colourless needles (m.p. 83°–84°). The isomeric coumarin melts at 105°. It was hydrolysed by alkali to 2-hydroxy-4-methyl-benzoic acid[13] (m.p. 175°). (Found : C, 77·9 ; H, 6·3 ; $C_{13}H_{12}O_2$ requires C, 78·0 ; H, 6·0 per cent.)

Cyclopenteno-(1' : 2' : 2 : 3)-1 : 4-*βα-naphtha-pyrone.*—A mixture of the ester (3 g.), β-naphthol (3 g.) and phosphorus pentoxide (6 g.) was heated on the water-bath for three hours, and at 120° for further half an hour. After treatment with water, the gummy residue was extracted with ether, the solution thoroughly washed with 5 per cent. alkali, dried, and the solvent recovered. The semi-solid mass thus obtained crystallised from alcohol in colourless needles (m.p. 165°–166°). The isomeric coumarin could not be prepared. (Found : C, 81·3 ; H, 4·9 ; $C_{16}H_{12}O_2$ requires C, 81·4 ; H, 5·1 per cent.) Its alkaline hydrolysis gave 2-hydroxy-α-naphthoic acid[14] (m.p. 156°) (rapid heating).

The styryl derivative, which was easily obtained by the usual method, crystallised from alcohol in very pale-yellow silky needles (m.p. 220°). (Found : C, 85·0 ; H, 5·1 ; $C_{23}H_{16}O_2$ requires C, 85·2 ; H, 4·9 per cent.)

We have great pleasure in thanking Dr. R. F. Hunter for his kind interest in this work.

Summary of Part III.

Chromones have been prepared by condensing cyclopentanone-2-carboxylate with phenol, *m*-cresol, *p*-cresol and β-naphthol in the presence of phosphorus pentoxide. The mechanism of the Pechmann and Simonis Reactions has been discussed.

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CONSTITUTION OF GOSSYPITRIN. AN ATTEMPT TO DEFINE THE POSITION OF THE GLUCOSE RESIDUE.

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Received May 25, 1937.

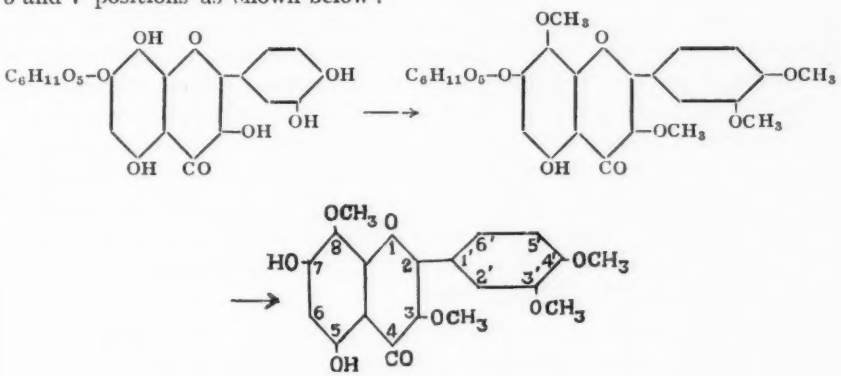
Gossypitrin, a glucoside of the anthoxanthin group of pigments, has been isolated from the Indian (*G. herbaceum* and *neglectum*) and the Egyptian *G. barbadense*) cotton flowers.[1,2] It is a monoglucoside of the flavonol gossypetin whose constitution was arrived at from its decomposition products by Perkin[3] and was established by synthesis by Baker, Nodzu and Robinson.[4] No attempt has till now been made to locate the position of the sugar group, but there exists sufficient information relating to the reactions of gossypitrin that enables a surmise to be made as to the probable position.

All known glycosides of the anthoxanthins fall into two definite groups : (1) the 7-glycosides and (2) the 3-glycosides. As a rule the sugar nucleus has not been found to be present in the hydroxy-phenyl portion of the molecule. Position 5 which seems to be considerably favoured in the anthocyanin group has not been found to be occupied by the sugar residue in the anthoxanthins. In his work on the constitution of the quercetin glycosides Perkin has shown that there exist definite differences between the 3- and 7-glycosides in regard to the following properties :—(1) reaction with lead acetate, (2) rate of hydrolysis with acids and (3) shades obtained with different mordants. Gossypitrin gives a deep red precipitate with lead acetate, is hydrolysed with difficulty by acids and gives deep shades with mordants thus showing that it is a 7-glucoside. Further it gives the gossypetone reaction, thereby indicating that the *p*-hydroxyl groups in 5 and 8 positions are free. The possibility of 7 and 8 positions being free thereby giving an orthoquinone does not seem to exist since quercetagetin which has hydroxyl groups in ortho-positions does not give this reaction.

An attempt has now been made to define the position of the glucose residue by methylating gossypitrin with diazomethane and after hydrolysing the methylated glucoside with acid obtaining a pentamethyl-gossypetin which could be identified. This method has been adopted very successfully for other cases by Herzig and Schönbach,[5] and Attree and Perkin.[6] At the beginning the question seemed to be simple since 7-hydroxy-3 : 5 : 8 : 3′ : 4′-pentamethoxy-flavone which should be expected as the product, if gossypitrin were a 7-glucoside, had already been made by Baker *et al.*[4] But

gossypitrin is now found to undergo only partial methylation with diazomethane though under the same conditions quercimeritrin undergoes complete methylation. One of the hydroxyl groups obviously remains unattacked since on hydrolysis a tetramethyl-gossypetin is obtained. The nature of this compound has been determined by the analysis of the compound itself by the preparation and analysis of the diacetyl derivative, and by the preparation of hexamethyl-gossypetin by further methylation.

Our present attempt has, therefore, not been successful. It is known that during methylation with methyl iodide or diazomethane of flavonols the hydroxyl in the 5 position is the most difficult to methylate.[7,8] It may, therefore, be reasonably assumed that the unreactive hydroxyl group in gossypitrin is the one situated in that position and it is possible that the final tetramethyl-gossypetin obtained by us has hydroxyl groups in the 5 and 7 positions as shown below :



Experimental.

Methylation of gossypitrin.—Gossypitrin (0·5 g.) was finely powdered, dissolved in excess of hot methyl alcohol (250 c.c.), cooled to room temperature and treated with an ethereal solution of diazomethane (2·0 g.) in small quantities at a time, more methyl alcohol being added simultaneously.[6] The solution became cherry-red, there was a slight evolution of nitrogen and the colour gradually disappeared. After leaving overnight, the ether was removed by distillation on a water-bath, more methyl alcohol added, cooled and again treated with an ethereal solution of diazomethane (2·0 g.) in the above manner. After leaving overnight, the ether and alcohol were removed completely on a water-bath. On adding a small amount of water an amorphous pale yellow solid separated out. Attempts to crystallise this solid from water or from dilute alcohol were unsuccessful.

Gossypitrin is sparingly soluble in alcohol. (300 c.c. of methyl alcohol are insufficient to keep 1·0 g. of it in solution in the cold.) With a view to test if the high dilution of the solution was responsible for the incompleteness of the methylation it was considered desirable to repeat the experiment with gossypitrin made into a thin paste with methyl alcohol. In this case, however, there was a little more rapid evolution of nitrogen than in the previous case. Partial methylation which was effected thus increased the solubility of the product in methyl alcohol. Methylation was then completed as above. The product, however, was identical with the one obtained above and gave rise to the same substance on hydrolysis.

The diazomethane required for these experiments was prepared from nitrosomethylurea and potash.[9]

Hydrolysis of the methylated glucoside. Isolation of a tetramethyl ether of gossypetin.—The uncrystallised product was refluxed with 2 per cent. sulphuric acid for four hours. The solid went into solution and deposited on cooling a yellow crystalline precipitate which was filtered and purified by dissolution in very dilute potash (deep yellow solution) and reprecipitation by passing in carbon dioxide. The product was left overnight, filtered and recrystallised from dilute acetic acid when it was obtained as yellow needles. It was recrystallised twice again from alcohol when it was obtained as needles which sintered at 225° and melted at 227–30°. (Found in air dried sample : C, 60·8, H, 4·9 and methoxyl, 32·8 ; $C_{19}H_{18}O_8$ requires C, 61·0, H, 4·8 and methoxyl, 33·2 per cent.)

Acetylation of the product of hydrolysis. Preparation of a diacetyl derivative.—A portion of the tetramethyl-gossypetin was dried and acetylated by boiling with acetic anhydride and sodium acetate and the product obtained recrystallised twice from dilute alcohol. It was obtained as fine colourless needles which sintered at 135° and melted at 142–43°. (Found in air dried sample : C, 60·5, H, 5·1 ; $C_{23}H_{22}O_{10}$ requires C, 60·3, H, 4·8 per cent.)

Methylation of the products of hydrolysis. Preparation of the hexamethyl ether of gossypetin.—Another portion of the hydrolytic product was dissolved in excess of potash and methylated with excess of dimethyl sulphate in the usual manner. In order to destroy the excess of dimethyl sulphate it was finally heated on a water-bath for half an hour. The product was then cooled and repeatedly extracted by shaking with cold ether. On removing the ether, a yellow solid was obtained which on crystallising twice from aqueous alcohol gave almost colourless fine needles, m.p. 170° (Perkin : Hexamethyl-gossypetin, m.p. 170–72°).

Summary.

An attempt has been made to fix the position of the glucose residue in gossypitrin by methylation with diazomethane and hydrolysis of the product. It has been found that methylation is incomplete, one hydroxyl group remaining unaffected, and thereby giving after hydrolysis a tetramethyl-gossypetin. This compound probably has the two hydroxyl groups in the 5 and 7 positions.

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STUDIES IN ADSORPTION ON GELS.

II. A Comparative Study of the Capillary Spaces in Gels of Silica and Alumina.

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The method of preparation of silica gel is known to affect the nature of the capillaries in the adsorbent. The chalky gel prepared by Holmes is known to contain much wider capillaries than the glassy variety obtained by Patrick. The total capillary volume in the former is nearly double that in the latter.[5] As has been stated in Part I of " Studies in adsorption on gels "[13] the temperature of activation of alumina gel affects its capillary space. A comparative study of the capillary volume of alumina gel activated at different temperatures was made with the aid of the McBain-Bakr quartz spring microbalance.

Experimental.

Construction of springs of quartz fibre.—The preparation of a spring of quartz fibre and its use in adsorption experiments have been studied by McBain and his co-workers.[6,7,8,9] They have employed a carbon rod for winding the spring. Cameron,[2] however, has employed a silica tube. It was found in this laboratory that better springs could be obtained when a silica tube is used. With a carbon rod the flame employed in bending the fibre, oxidises the carbon and gives the rod a rugged surface. Owing to the greater heat conductivity of carbon, the heat of the flame does not get properly localised. This results in poor bending of the fibre. To overcome this defect Pidgeon[11] has used a fluted carbon rod with longitudinal grooves. When a silica tube is employed the heat of the flame can be localised and a winding of the fibre quite close to the tube secured. Corners in the spring may thus be avoided.

The production of springs having equidistant coils is a matter of some difficulty. Such springs have been prepared in this laboratory with the aid of an automatic winding device.[3] In the absence of an automatic device satisfactory springs can be obtained if the tube employed has on its surface, a helical impression. This is obtained by rotating the rod in a lathe while the sharp edge of a glass-cutting knife is directed against the tube. In contact with the flame the scratch appears brighter than the silica surface and the helical impression can therefore be easily traced while winding.

A conical shaped bucket of thin gold sheet attached to the spring by means of silica fibres, was employed for holding the adsorbent. When dealing with fine powders it was found necessary to cover the bucket with a lid of thin gold sheet.

Thermostat.—To maintain the adsorbent at a constant temperature an air thermostat was used as shown in Fig. 1. Efficient circulation of heated

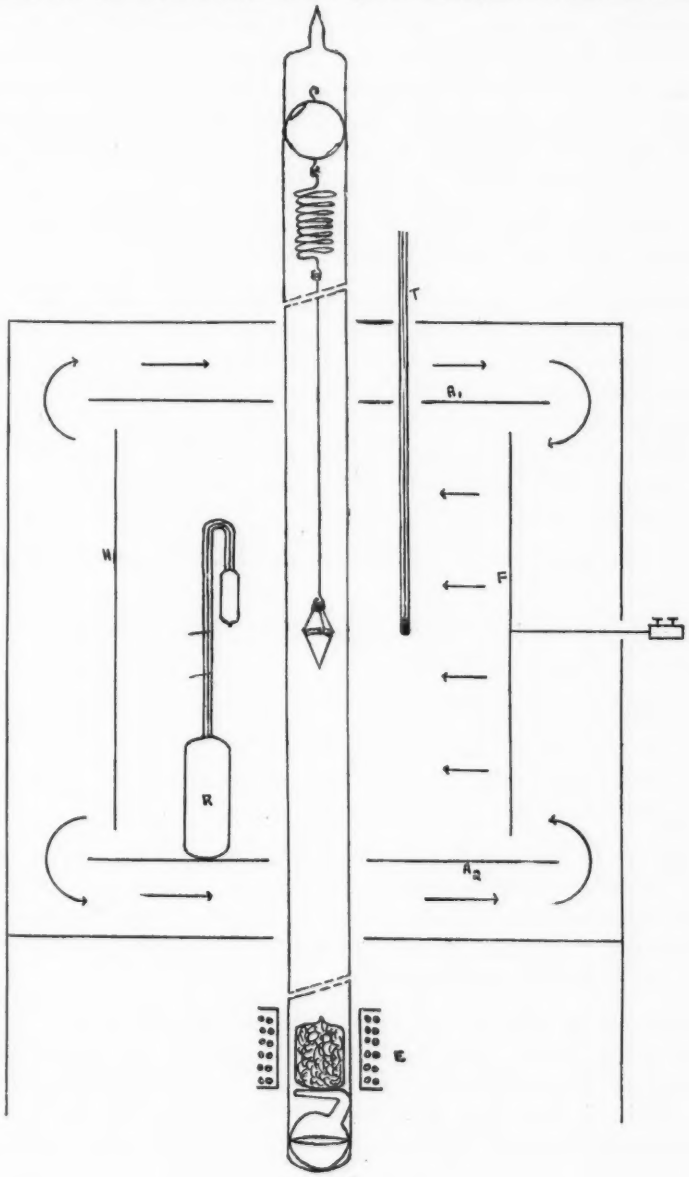

FIG. 1.

air was secured by employing the fan F. The heater H was made of heating mats. The thermo-regulator R contained mercury in vacuum in order to avoid fouling and had a temperature adjustment similar to that in a Beckmann thermometer.

The lower portion of the sorption tube containing the liquid was enclosed in a water thermostat. The thermostatic device described by Fox and Mankodi[4] was employed when the liquid had to be maintained at a temperature lower than that of the laboratory.

A Cenco travelling microscope reading correct to 0·001 cm. was used to measure the stretch of the spring during adsorption.

Materials.—Two varieties of silica gel were employed. The "glassy" variety was obtained by the method described by B. S. Rao and K. S. G. Doss.[12] The chalky gel was prepared by adding 220 c.c. of 2 N nickel chloride, to 2,000 c.c. of potassium silicate (Density, 1·02) the latter being stirred vigorously. The precipitate was allowed to settle, separated, washed with dilute hydrochloric acid in the beginning and with distilled water subsequently and the gel dried. The opaque gel was powdered and particles 1 to 2 mm. in diameter were used.

Alumina gel employed had been prepared by the method described in Part I.[13]

Pyridine.—Merck's "extra pure" pyridine was treated with solid potassium hydroxide and distilled.

Procedure.—Glass bulbs of 1·5 c.c. to 2 c.c. capacity were filled with the liquid according to the procedure described by McBain and co-workers.[10]

The bulb containing the liquid was placed in a glass tube (3′ long, 1″ diameter) as shown in Fig. 1.

The gel was activated *in situ* by heating for 6 hours at 450° C. in an electric furnace, the tube being evacuated by the mercury vapour pump backed by the Cenco "Hyvac" pump. After activation of the gel the sorption tube was sealed off from the pump. The stretch of the spring for the activated gel was then measured.

The sorption tube was next introduced into the thermostat the travelling microscope focussed to the hook of the spring. The lower end of the sorption tube was cooled in a mixture of solid carbon dioxide and alcohol. Such cooling is necessary to prevent the sudden rush of vapour into the adsorption chambers as this throws the bucket off the spring. After cooling

for half an hour, the bulb containing the liquid was broken open, by employing an electro-magnetic device (E). The thermostatic bath was then kept in position to keep the bulb at the required temperature. The course of adsorption was studied by measuring the stretch of the spring at frequent intervals with the aid of the travelling microscope.

A corresponding pressure of 0·53 was maintained. To secure this, water had to be kept at 28°·5 C. and pyridine at 27°·7 C.

Results are given in Tables I to V and shown in Figs. 2 and 3.

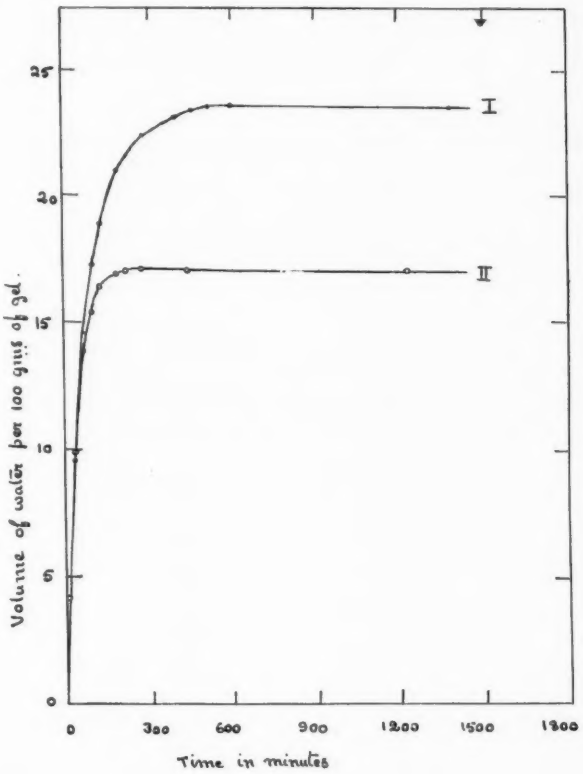

FIG. 2.

I. Glassy silica gel and water. II. Chalky silica gel and water.

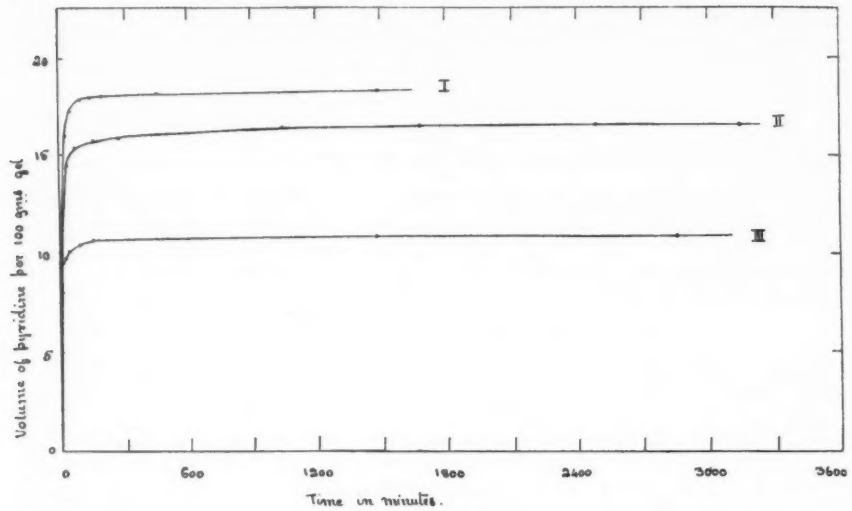

FIG. 3.

I. Alumina gel (activated at 500° C.) and pyridine.
II. Alumina gel (activated at 400° C.) and pyridine.
III. Alumina gel (activated at 850° C.) and pyridine.

TABLE I.

Adsorption of water on "glassy" silica gel activated at 450° C.

Time in minutes	Vol. in c.c. of H_2O at 40° C. held by 100 gm. of gel
30	9·50
60	14·51
90	17·28
120	18·91
180	20·98
270	22·33
390	23·04
450	23·38
510	23·57
590	23·42
1380	23·42

TABLE II.

Adsorption of water on "chalky" silica gel activated at 450° C.

Time in minutes	Vol. in c.c. of H_2O at 40° C. held by 100 gm. of gel
30	9·89
60	13·91
90	15·45
120	16·39
180	16·93
210	17·06
270	17·19
435	17·13
1230	17·13

TABLE III.

Adsorption of pyridine on alumina gel activated at 400° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	14·41
60	15·44
150	15·73
270	15·81
1050	16·51
1680	16·66
2490	16·66
3150	16·66

TABLE IV.

Adsorption of pyridine on alumina gel activated at 500° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	16·13
45	17·31
90	17·98
140	18·04
195	18·11
455	18·28
1485	18·42

TABLE V.

Adsorption of pyridine on alumina gel activated at 850° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	9·80
45	10·18
90	10·39
150	10·64
1485	10·79
2865	10·88

The activation of alumina gel at 850° C. could not be accomplished *in situ*. The gel was activated in an electric furnace in a current of dry air and then carefully transferred to the sorption tube.

Discussion.

Chalky gel has been known to have higher capillary volume than glassy variety, but to be poorer in fine capillaries. Liquid in fine capillaries has smaller vapour pressure than that held in broader ones. So in the glassy gel (which has fine capillaries) a larger amount of liquid (23·4 per cent.) is held at a corresponding pressure of 0·53 than in the chalky variety which retains only 17·1 per cent. At the saturation pressure, however, the chalky gel holds weight for weight nearly twice the volume of liquid retained by the glassy variety.

There has been considerable difference in the periods required for the attainment of equilibrium with the two gels. The glassy gel takes for water about 8 to 9 hours whereas chalky gel attains equilibrium within about 3½ hours. This difference in the rates of adsorption is to be attributed to the size of the capillaries. The finer the capillaries greater is the time required for the attainment of equilibrium. According to Burrage[1] "the water condensed at the mouth of the smaller capillaries will retard free access into the interior and the capillaries require considerable time for complete filling."

The results on the adsorption of pyridine vapour by alumina gel activated at 400° C., 500° C. and 850° C. are noteworthy. The variation of the total capillary volume with the temperature of activation has already been indicated in Part I.[13] At saturation pressures the maximum adsorptive capacity is exhibited by gel activated at 850° C. At the corresponding pressure of 0·53 however this gel can take up only 10·9 per cent., though its total capillary volume is nearly 29·0 per cent. Gels activated at 400° C. and 500° C. have taken up (at corresponding pressure of 0·53) 16·7 per cent. and 18·4 per cent. though their total capillary volumes are 18·5 per cent. and 21·6 per cent. respectively. It is to be noted that though the total capillary volume rises with an increase in the temperature of activation, there is no similar increase in the volume of liquid adsorbed at a corresponding pressure of 0·53, the gel activated at 500° C. having higher adsorption than the other two gels. This shows that the capillaries in the gel activated at 850° C. are broader and do not get filled up to the same extent as the capillaries in the other two varieties. The effect of increasing the temperature of activation from 400° C. to 500° C. seems to be an increase in the total capillary space without any corresponding broadening of capillaries. Beyond 500° C. however, an increase in temperature of activation causes a considerable widening of pores. This is probably to be attributed to the loss of water from the monohydrate of alumina at temperatures above 500° C.

Summary.

A microspring balance of quartz fibre of the McBain-Bakr type has been used for studying adsorption of vapours of water and pyridine on gels of silica and alumina.

The difference in adsorption on " glassy " and " chalky " gels of silica has been accounted for, by the wider capillaries in the latter.

Adsorption of pyridine on alumina gels activated at 400° C., 500° C. and 850° C. has been studied. The differences noticed are attributed to the variation in capillary size.

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INHIBITION OF FLUORESCENCE.

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It is well known that the brilliant fluorescence of a fluorescent solution can be inhibited by the presence of certain ions. An aqueous solution of quinine sulphate does not fluoresce in presence of sufficient concentration of the halide ions. The inhibition is also brought about by the fluorescent molecule itself as is shown by the fact that the ratio of fluorescent intensity to concentration of a fluorescent substance is not constant, but falls off with increase in concentration. Brunninghaus[1] was the first to attempt at an explanation of the self-inhibition of fluorescence; he suggested that it is caused by the absorption of light; the increase in concentration, though brings about an increase in fluorescence, there will be an increase in absorption and the fluorescent intensity is therefore given by $I = k_1 x e^{-k_2 x}$ where x is the concentration of the fluorescent substance. Though this was in accordance with the measurements made on the cathodo-luminiscence of manganese in calcium phosphate it is unable to explain recent work.[2] Perrin[13] explained the phenomenon on the basis of protective action. Perrin's idea has been successfully made use of by Merritt[2] to explain quantitatively the variation of fluorescent power with concentration. Jette and West[3] have suggested that the self-inhibition is caused by collisions of second kind between the photo-excited and the ordinary fluorescent molecules. It is also to be noted that a " Perrin protection " becomes more or less identical with a collision of the second kind if the former is assumed to take place at molecular distances. Jette and West have also accounted for the inhibition by ions as being caused by collisions of the second kind between the photo-excited fluorescent molecules and the inhibitors. The object of the present paper is to put the suggestion of Jette and West into a quantitative form and examine its applicability to the existing experimental data.

Inhibition by Electrolytes.

When a solution of a fluorescent substance is exposed to light, a stationary state is set up, so that, Rate of excitation = Rate of emission + Rate of inhibition. The rate of excitation is equal to $k_1 n_f$ where n_f is the concentration of the fluorescent substance and k_1 is a proportionality constant.

The rate of emission is proportional to n'_f the concentration of the photo-excited molecules in the stationary state and is equal to $k_2 n'_f$.

The rate of inhibition (assuming that it is due to collisions of the second kind) is equal to $k_3 \delta n'_f n_i$, where n_i is the concentration of the inhibitor, δ is the efficiency of the inhibitor in bringing about inhibition and k_3 is a pure kinetic theory constant. Thus,

$$k_1 n_f = k_2 n'_f + k_3 n'_f n_i \delta$$

or

$$k_2 n'_f = k_1 n_f - \frac{k_1 k_3 \delta n_f n_i}{k_2 + k_3 \delta n_i}$$

At small concentrations of the inhibitor, the fluorescent intensity $k_2 n'_f$ is given by the equation

$$k_2 n'_f = k_1 n_f - \frac{k_1 k_3 \delta n_f n_i}{k_2}$$

In the absence of inhibitor, the fluorescent intensity is obviously equal to $k_1 n_f$. So, the percentage fall in intensity due to the presence of inhibitor at small concentrations is given by $p = \dfrac{100 k_3 n_i \delta}{k_2}$ (1)

Here k_2 is the reciprocal of the average life of the fluorescent molecule in the excited state[4] and is usually of the order $\dfrac{1}{5 \times 10^{-9}}$ or 2×10^8 sec.$^{-1}$ The value for k_3 can be obtained as follows :—

The rate at which two types of molecules initially not in contact come into contact is given by the equation

$$Z = 4\pi (D_1 + D_2) n_1 n_2 (r_1 + r_2)$$

where D_1, D_2 are the diffusion coefficients of the molecules, n_1, n_2 are the concentrations of molecules of the first and the second types and r_1 and r_2 are the radii of the molecules. (Here we are adapting Smoluchowsky's equation for rapid coagulation for the present case.) Substituting for D_1 and D_2 the appropriate expressions of Einstein, one gets

$$Z = 4\pi \frac{RT}{N} \cdot \frac{1}{6\pi\eta} \left\{\frac{1}{r_1} + \frac{1}{r_2}\right\} (r_1 + r_2)\ n_1 n_2$$

$$= \tfrac{2}{3} \frac{RT}{N\eta} \frac{(r_1 + r_2)^2}{r_1 r_2} n_1 n_2$$

where R is the gas constant, T the absolute temperature and N the Avogadro number. Applying the formula, for the inhibition process, one gets

$$k_3 n'_f n_i = \tfrac{2}{3} \frac{RT}{N\eta} \frac{(r_f + r_i)^2}{r_f r_i} n'_f n_f$$

or

$$k_3 = \frac{2}{3}\frac{RT}{N\eta}\frac{(r_f+r_i)^2}{r_f r_i} \qquad (2)$$

Combining equations 1 and 2 and putting $k_2 = 2 \times 10^8$ one gets,

$$p = \frac{2}{3}\frac{RT}{N\eta}\frac{(r_f+r_i)^2}{r_f r_i}\cdot\frac{n_i\delta}{2\times 10^8}\times 100 \qquad (3)$$

It is to be pointed out that $\frac{(r_f + r_i)^2}{r_f r_i}$ has a value of the order of 6. If $\frac{n_i}{N}$ is equal to $2{\cdot}5 \times 10^{-6}$ moles per c.c. one gets for the inhibition efficiency, $\delta = 0{\cdot}08\,p$.

If $\frac{n_i}{N}$ is $2{\cdot}5 \times 10^{-5}$ moles per c.c. one gets $\delta = 0{\cdot}008\,p$.

Thus, the efficiency of inhibitors can be calculated from the percentage fall in the fluorescent intensity brought about by the inhibitor. Tables I and II contain the values calculated on this basis from the data of Jette and West.

TABLE I.

Efficiency of inhibitors in inhibiting the fluorescence of quinine sulphate solutions.

Inhibitor	Efficiency
NO_3'	0·004
SO_4''	0·056
CH_3COO'	0·60
C_2O_4''	0·84
Cl'	1·9
Br'	2·2
CNS'	2·4
I'	2·8
Ag^+	0·36

TABLE II.

Efficiency of inhibitors in inhibiting the fluorescence of sodium fluoresceinate solutions.

Inhibitor	Efficiency
Br'	0·012
CNS'	0·176
I'	0·232
Ag^+	0·40

TABLE III.

Efficiency of auto-inhibition.

Fluorescent substance	Efficiency
Quinine sulphate ..	1700
Aniline-iodeosine ..	550

Auto-Inhibition by the Fluorescent Ions.

The efficiency of fluorescent ions as self-inhibitors can be worked out, as follows, from fluoremetric data obtained by Desha.[5] In fluoremetry, ultra-violet rays from a mercury arc filtered from most of the visible radiation are used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kobernephelometer. The intensity of scattered light, as observed in the eye-piece of the instrument is equalised in the usual way by adjusting the heights of the columns of solutions included in the fields of view of the optical plungers. Let us now calculate the fluorescent intensity due to a column of liquid of unit height below the optical plunger. Proceeding as before one gets in the stationary state,

$$k_1 n_f = k_2 n'_f + k_3 n_f n'_f \delta$$

or

$$k_2 n'_f = k_1 n_f - \frac{k_1 k_3 n^2_f \delta}{k_2 + k_3 n_f \delta}$$

For small concentrations of the fluorescent substance $k_2 \gg k_3 n_f$ so that, the fluorescent intensity due to a unit column is given by

$$k_2 n'_f = k_1 n_f - \frac{k_1 k_3}{k_2} n^2_f \delta$$

If c is the concentration of the fluorescent substance in grams per c.c. and M_f is its molecular weight, $n_f = \frac{cN}{M_f}$; so that, the fluorescent intensity due to a unit column becomes $\frac{k_1 N}{M_f} c\ (1 - \gamma c)$ where $\gamma = \frac{k_3 N \delta}{k_2 M_f}$. The fluorescent intensity due to a column of solution of height h after applying correction for absorption of scattered light by successive layers becomes

$$\frac{k_1 N}{M_f} c(1-\gamma c) \int_{y=0}^{y=h} e^{-qcy}\, dy$$

where q is the absorption coefficient for the solute. On integration, one gets, for the fluorescent intensity,

$$\frac{k_1 N}{M_f} c(1 - \gamma c) \frac{\{e^{-qch} - 1\}}{-qc}$$

As the solutions are dilute, $e^{-qch} - 1$ can be put equal to $-qch$ so that the fluorescent intensity becomes,

$$\frac{k_1 N}{M_f} ch(1 - \gamma c)$$

This is kept constant in all fluoremetric measurements, so that

$$ch\ (1 - \gamma c) = \text{constant} \qquad (4)$$

Equation 4, it is to be pointed out, is of the same form as the one formerly derived by the author.[6] This has been shown to be in fair agreement with the fluoremetric data obtained by Desha.[5]

As shown before, $k_2 = 2 \times 10^8$ sec.$^{-1}$ and k_3 works out to be $\frac{8}{3} \frac{RT}{N\eta}$ so that

$$\gamma = \frac{8}{3} \frac{RT}{N\eta} \cdot \frac{N\delta}{2 \times 10^8 M_f}$$

or

$$\delta = \frac{3 \times 10^{+8} \eta \gamma M_f}{4RT}$$

Putting proper values for η and T one gets $\delta = 3 \times 10^{-5} \gamma M_f$. γ is calculated from the experimental results by the equation $\gamma = \frac{c_1 h_1 / c_2 h_2 - 1}{c_1 - c_2}$, where h_1 and h_2 are the heights corresponding to the concentrations c_1 and c_2 respectively.

For quinine sulphate: $c_1 = 1 \times 10^{-6}$; $c_2 = 0{\cdot}5 \times 10^{-6}$; $h_1 = 19{\cdot}5$; $h_2 = 36{\cdot}6$; $M_f = 436$.

Thus $\delta = 1700$.

For aniline iodeosine: $c_1 = 4 \times 10^{-6}$; $c_2 = 2 \times 10^{-6}$; $h_1 = 16{\cdot}00$; $h_2 = 30{\cdot}90$; $M_f = 955$.

Thus $\delta = 550$.

Discussion.

An examination of the tables shows that inhibitors fall into three broad classes: (*a*) ions like NO_3' and SO_4'' which have very low inhibition efficiencies, (*b*) ions like Cl′, Br′, I′, CNS′ which have many of their collisions effective in bringing about inhibition and (*c*) the fluorescent ions themselves, which have efficiencies exceeding unity by several orders.

A simple kinetic interpretation can be given for the inhibition by ions of class (*b*). The departure of the efficiency from unity can be accounted for by the orientation requirements for an effective collision. The low efficiencies exhibited by ions of class (*a*) may be caused by the small probability of energy transfer during a collision. The very high efficiencies exhibited by the fluorescent ions cannot be accounted for by any simple kinetic theory mechanism. In all these calculations, the effect of interionic attraction has been neglected. Taking this into account on the lines suggested by Moelwyn-Hughes[7] the present author has calculated approximately the corrections to be applied; if it is applied for the fluorescent ions, it further increases the value of inhibition efficiency so that a consideration of the electrical forces does not remove the difficulty. A similar difficult situation arises in the interpretation of quenching of fluorescence in the gaseous phase. To overcome the difficulty E. Gaviola[8] suggests "The simplest way seems then to maintain the gas-kinetic radius of the normal also for the excited atom in all cases in which doing so, the efficiencies turn out to be smaller than unity and when not, to assume a radius for the excited atom, larger than the gas-kinetic one, for each particular case, so that efficiencies in each case are unity.....This assumption is, of course, also arbitrary." On the other hand, our own equation for the inhibition in liquid phase shows that the extent of inhibition is *not* sensibly dependent on the radius of the fluorescent molecule; for, an increase in the radius of the molecule, though increases the volume swept by the molecule per unit distance travelled, it also brings about a diminution in the diffusion rate to a corresponding extent. So the present author is of opinion, that the high collision efficiences observed by the present author (and possibly also those observed by

Gaviola) can best be accounted for by postulating a deep minimum in the potential energy curve for the approach of the fluorescent molecules. Whether this minimum is to be interpreted as polymerisation leads us to consider the question with reference to the controversy between Hildebrand and Glockler.[9] Glockler is tempted to regard any configuration of two or more atoms, simple molecules or radicals which exhibit a potential minimum as a case of complex formation. On the other hand, Hildebrand believes that formation of complexes can be postulated only when the existing interaction between the simpler molecules is higher than the usual Van der Waals forces. Thus, it is of interest to calculate the magnitude of the depth of the minimum in the potential energy curve. If the interaction is not very high (so that the concentration of such complexes is low), the energy of interaction ΔH can be calculated[10] by the equation $c_{A_2} = c_A^2 \, e^{\Delta H/RT}$ where c_{A_2} is the concentration of the di-mer of the fluorescent substance and c_A is the total concentration. (It is assumed here that the fluorescent substance is present only as monomer and di-mer.)

Putting $c_A = \frac{c}{M_f}$ and $c_{A_2} = \frac{\gamma c^2}{2M_f}$

one gets

$$e^{\Delta H/RT} = \frac{\gamma c^2}{2M_f} \cdot \frac{M_f^2}{c^2} = \frac{\gamma M_f}{2}$$

Thus

$$\Delta H = RT \, ln \, \frac{\gamma M_f}{2}$$

The values of the energy of interaction works out to be of the order of 10,500 cals. per mole for quinine sulphate as well as for aniline iodeosine. The values indicate very deep minima and are comparable with the heats of dissociation of well-known complexes. (*Cf.* Heats of dissociation: Hg_2, 3,500 cals.; N_2O_3, 10,300 cals; N_2O_4, 14,600 cals. *Vide* Reference No. 11.) Indications are not wanting that such molecules of high molecular weight have a tendency for association in aqueous solution. In fact, the hypothesis of polymerisation is the only one which can account satisfactorily for inhibition in solid solutions.[12] Thus, the evidence from fluoremetric data is in favour of polymerisation as being the cause of self-inhibition of ultra-violet fluorescence of quinine sulphate and aniline-iodeosine.

Summary.

The data obtained by Jette and West regarding inhibition of fluorescence have been examined with a view to get at the mechanism of the inhibition process. The results show that inhibitions by ions such as Cl′,

Br′, I′, etc., can be interpreted on the basis of collisions of the second kind. The auto-inhibition of fluorescence, however, as shown by a critical examination of fluoremetric data cannot be explained on the basis of collisions of the second kind ; it is found necessary to postulate polymerisation of the fluorescent substance, in order to explain the self-inhibition of the ultra-violet fluorescence of quinine sulphate and aniline iodeosine solutions.

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SELECTIVE ADSORPTION ON SILICA GEL FROM PYRIDINE-ALCOHOL MIXTURES.

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Introduction.

Selective adsorption on silica gel from binary mixtures of liquids has been studied by several workers.[1, 3, 4, 5, 6] The theoretical aspect of the subject has been thoroughly discussed by Doss and Rao.[1] They have shown that the so-called "apparent adsorption" is more significant than "true adsorption". They have therefore designated apparent adsorption by the more appropriate term "selectivity". The latter is given by the expression $\frac{M\ (c_1 - c_2)}{100g}$ where M is the mass of the binary mixture used, g is the mass of the adsorbent, c_1 is the initial concentration of one of the components (in weight per cent.) in the binary mixture and c_2 is the final concentration of the same component in bulk solution which is in equilibrium with the adsorbent. The curves connecting selectivity with equilibrium concentration may be U-shaped or S-shaped. The special significance of the S-shape has been pointed out by Doss and Rao.[1] The study of adsorption on silica gel from pyridine-alcohol mixtures was taken up from this point of view.

Experimental.

Preparation of activated silica gel and the technique of adsorption measurements have been described in the former contributions.[1,2] The ethyl alcohol used was obtained by distilling absolute alcohol over calcium. Kahlbaum's purest pyridine twice distilled over solid potassium hydroxide was employed. The pyridine-alcohol mixtures were prepared by weighing and their refractive indices were determined by employing the Pulfrich Refractometer. The changes in concentration brought about by adsorption were determined by measuring the refractive index and interpolating with reference to the refractive index-concentration curve.

Results.

(1) *Refractive indices of pyridine-alcohol mixtures.*—The values obtained for the refractive indices of binary mixtures after correcting for the zero shift of the instrument and temperature of the prism are given in Table I.

(2) *Selective adsorption on silica gel.*—The values for selectivity obtained for the pyridine-alcohol-silica system are given in Table II and Fig. 1.

TABLE I.

Refractive index of pyridine-alcohol mixture.

Temperature : 23°·37 C. ± 0°·03.

Gm. of pyridine per 100 gm. of mixture	Refractive Index
0·00	1·35972
10·07	1·37289
21·00	1·38732
29·63	1·39926
39·92	1·41355
49·99	1·42814
60·03	1·44289
69·93	1·45801
79·95	1·47387
89·56	1·48971
100·00	1·50779

TABLE II.

Selectivity for pyridine-alcohol-silica system.

Equilibrium concentration in weight per cent. pyridine	Selectivity for pyridine
9·00	0·0219
18·7	0·0330
27·2	0·0346
37·7	0·0314
48·0	0·0254
58·6	0·0193
69·3	+ 0·0102
80·0	— 0·0010
81·7	— 0·0033
84·1	— 0·0037
89·8	— 0·0059

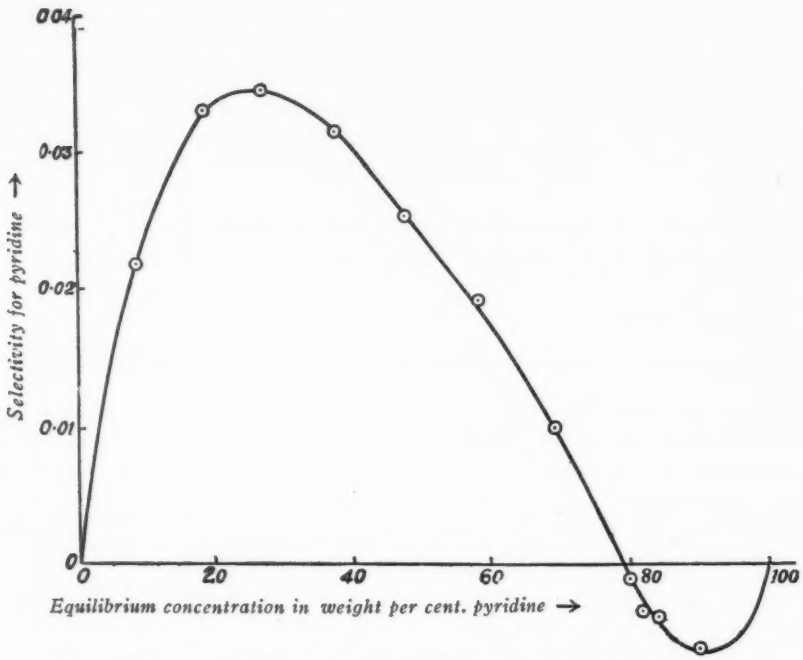

FIG. 1. Selective adsorption on silica gel from pyridine alcohol mixtures.

Discussion.

The pyridine-alcohol mixtures are found to give an S-shaped curve. After a consideration of the several factors underlying selective adsorption, Doss and Rao suggested that the S-shaped curve is caused by the preferential adsorption of a complex of intermediate composition. The complex preferentially adsorbed should have the composition of the liquid having zero selectivity. For the adsorption of pyridine-water mixtures (1), the complex closely corresponds to C_5H_5N, H_2O and for acetone-water mixtures it corresponds to $CH_3 \cdot CO \cdot CH_3$, H_2O. In the present case the complex consists of 78·5 per cent. pyridine corresponding to 2 C_5H_5N, EtOH. Though a corresponding compound is not known to form in solutions its formation at the surface of the adsorbent may be understood in view of the strong residual field that is presented by the surface of solids.

It is found further that the maximum selectivity for pyridine is higher than the maximum selectivity for alcohol. Following F. London,[7] adsorption may be interpreted as due to the " deeper lying quantum states " which

are formed when the molecules of the adsorbent and the adsorbate are brought together. The formation of such quantum states would have a higher probability, in cases where there would be a higher mutual deformation of the molecules. One would expect the weakly acidic silica molecules at the surface of the adsorbent to undergo more of deformation by the influence of the weakly basic pyridine molecules than by the neutral alcohol molecules. This may explain the observed high adsorption of pyridine by silica.

Summary.

Refractive indices of pyridine-ethyl alcohol mixtures have been measured at 23°·37 C. The selective adsorption on silica gel from pyridine-ethyl alcohol mixtures has been measured over the entire range of concentration. The selectivity concentration curve is found to be of the S-type. Evidence is adduced to show that an adsorption compound C_5H_5N, 2 EtOH is formed at the interface.

In conclusion the authors wish to thank Professor B. Sanjiva Rao for his interest in the work.

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PHYSICO-CHEMICAL INVESTIGATIONS ON VARIETAL DIFFERENCES IN RICE.

I. Sorption and Desorption of Water Vapour by Rice Grains.*

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Introduction.

It is well known that different varieties of rice exhibit marked differences on cooking. The problem of varietal differences in rice is one of considerable importance as rice constitutes the chief article of diet of the majority of Indians and of several other Eastern nations.

The object of the present investigation was to correlate with quality the physico-chemical properties of rice. The information so far available on the subject is scanty. A great deal of parallel work has been carried out by Görtner[1] and others on wheat and wheat starches. Some work on rice has been carried out by Warth[2] and others at Pusa and by Japanese workers at Tokyo. It has been found that the quality of rice cannot be satisfactorily correlated with chemical composition. Tetsudaro Tadokoro[3] and his collaborators have attempted a study of the chemical differences between starch from glutinous and non-glutinous rices. They conclude that under similar conditions, the viscosity of glutinous rice starch suspensions is higher. The ash from glutinous rice is richer in silicate than in phosphate while the non-glutinous rice yields an ash richer in phosphate than in silicate.

Several important contributions to the colloid chemistry of starch have been made by Samec.[4] According to him starch granules consist of two different chemical entities—amylose and amylopectin, the latter being chiefly responsible for the colloidal behaviour of starch sols.

Work done in this laboratory by Sanjiva Rao[5] and his co-workers has given indications of the presence of fine capillaries in rice grains. Attempts to correlate the quality of rice with the capillary space available for sorption have not hitherto been successful. It was noticed that suspensions of rice powder in dilute alkali exhibit marked increase in viscosity with time. But the viscosity changes could not be correlated with quality. As cooking of rice is chiefly associated with imbibition of water, it was felt that a study of the sorption and desorption of water vapour by rice would throw light on its quality.

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* The matter presented in this communication formed part of the thesis submitted by K. Subbaramiah in partial fulfilment of the requirements of the M.Sc. Degree of the Mysore University.

Experimental.

(*a*) *Dehydration of rice grains by heating.*—Rice grains from seven different samples of paddy, aged as well as newly harvested, were kept in weighing bottles of identical size and shape, and were heated in a special type of steam oven which enabled the passage of a current of dry air over the rice during dehydration. The weighing bottles were removed at intervals, weighed, and the loss in weight due to dehydration noted. It was found in general that the dehydration was rapid for the first six to eight hours and then slowed down by a very appreciable extent. In some cases even seventy hours' heating was insufficient to bring about complete dehydration. It was noticed that rice from paddy stored for nearly two years lost more water than rice from freshly harvested paddy. In all these experiments the paddy was dehusked by gentle rubbing between two asbestos cement plates.

The results obtained are given in Table A. The percentage dehydration is expressed with reference to the *final* weight of the rice grains when dried.

(*b*) *Dehydration of rice by vacuum desiccation.*—Dehydration of rice grains in a vacuum desiccator over phosphorus pentoxide (Fig. 1), was also

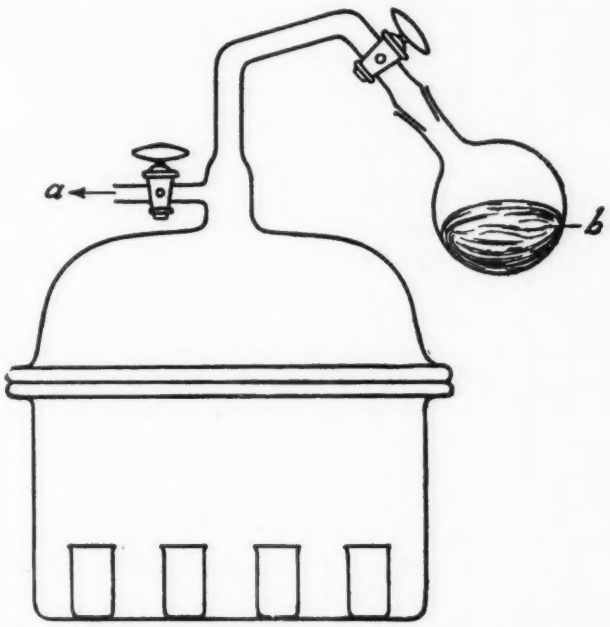

FIG. 1.

a = Lead for evacuation. *b* = Phosphorus pentoxide with glass wool

TABLE A.

Dehydration of rice grains on heating in a steam oven in a current of dry air.

Time of heating	Percentage dehydration observed													
	Mysore Kaddi		Coimbatore Sanna		Nagpur Sanna		Doddabyra		Doddabele		Jeddu Hegge		Walya	
	new	old	new	old	new	old	new	old	new	old	new	old	new	old
1 hour ..	5·03%	8·31%	4·81%	5·71%	5·59%	7·13%	4·83%	5·37%	4·59%	5·35%	4·59%	5·52%	4·12%	6.13%
2 hours ..	6·47	10·09	6·14	7·13	6·78	8·35	5·98	7·06	5·93	6·73	6·03	7·21	4·78	6·95
3 hours ..	7·20	10·85	6·72	7·75	7·31	8·99	6·68	7·70	6·63	7·48	6·77	8·02	5·42	7·70
4 hours ..	7·73	11·36	7·15	8·16	7·69	9·43	7·33	8·47	7·07	7·92	7·33	8·60	5·98	8·25
8 hours ..	8·77	12·44	8·14	9·10	8·69	10·38	8·18	9·32	8·17	8·96	8·36	9·58	6·80	9·05
24 hours ..	9·75	13·43	9·12	10·06	9·45	11·14	9·00	10·10	9·15	9·90	9·52	10·60	8·10	10·08
2 days ..	10·12	13·80	9·56	10·49	10·08	11·71	9·80	10·79	9·86	10·50	9·96	10·97	8·65	10·40
3 days ..	..	..	..	..	..	..	..	..	10·14	10·70	10·20	11·21	9·06	10·60

studied. The desiccator was kept in an air-thermostat at 32° C. Measurements were made at intervals. The dehydration was found to be very slow and incomplete even after four days. As in the case of dehydration on heating, the aged samples were found to lose more water than newly harvested ones. The values obtained are shown in Table B.

TABLE B.

Dehydration of rice grains in a vacuum over phosphorus pentoxide.

Period of dehydration	Percentage dehydration observed					
	Doddabyra		Coimbatore Sanna		Nagpur Sanna	
	new	old	new	old	new	old
70 minutes	1·29%	1·97%	1·34%	2·14%	1·58%	3·41%
165 minutes	2·34	3·18	2·42	3·40	2·55	4·81
4 hours	2·98	3·87	3·10	4·07	3·18	5·54
6 hours	3·61	4·54	3·82	4·74	3·81	6·20
15 hours	4·50	4·96	4·67	5·65	4·68	7·03
29 hours	5·30	5·58	5·42	6·34	5·39	7·72
50 hours	5·64	6·31	5·72	6·59	5·68	7·88
72 hours	5·97	6·63	6·02	6·89	6·01	8·18
108 hours	6·50	7·19	6·54	7·39	6·54	8·70

(*c*) *Isothermal desorption and sorption of water vapour by rice.*—The isothermal desorption and sorption of water vapour by four varieties of rice grains (Mysore Kaddi, Coimbatore Sanna, Doddabyra and Doddabele, all harvested in 1933) was studied using a modification of the sorption microbalance described by McBain and Bakr[6] (Fig. 2). The grains were kept in a gold bucket attached to the silica spring inside the sorption tube. By means of a thermostatic arrangement these grains were maintained at 40° C. The sorption tube was evacuated for half an hour with a Cenco Hyvac pump, and then for four hours with a Langmuir mercury vapour diffusion pump. The rate and the extent of dehydration during evacuation was followed with a travelling microscope. After evacuation, the dehydration was continued over phosphorus pentoxide until it became exceedingly slow. At this stage the phosphorus pentoxide bulb was shut off and water vapour, saturated at 25° C., was let into the sorption tube. The rate of

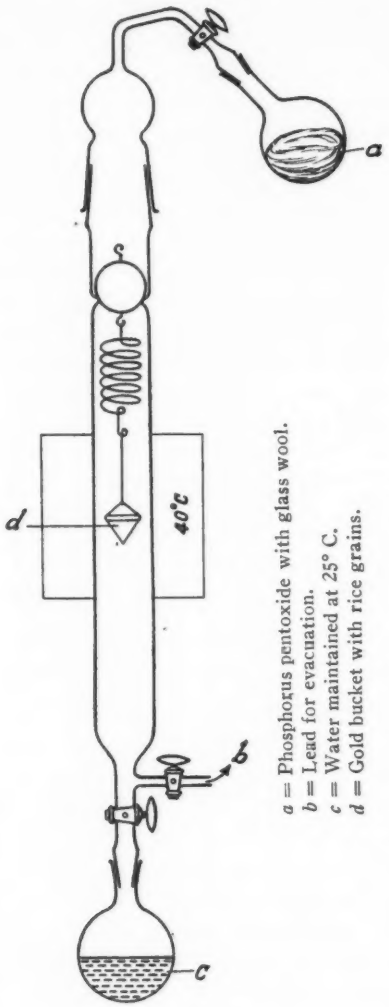

FIG. 2.

hydration of the grains at 40° C. was studied as before. Hydration was found to be complete in 24 hours. The grains were then allowed to cool down to the room temperature of 28–30° C. and the hydration at this temperature measured. The results obtained are shown in Tables C and D and Figs. 3 and 4.

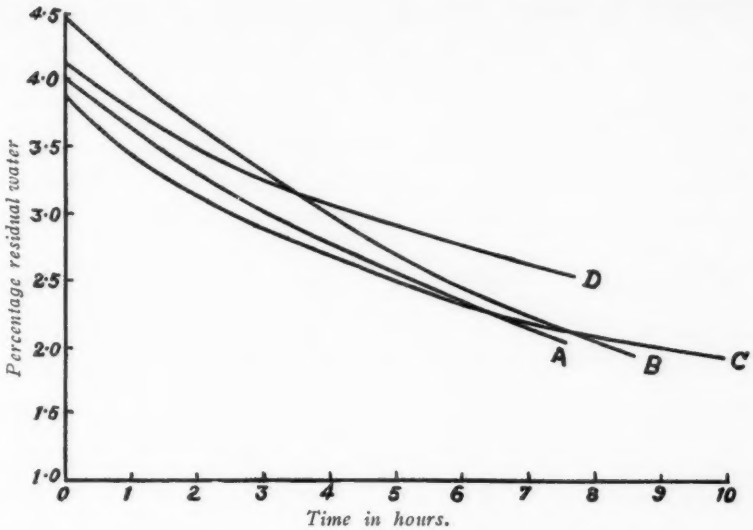

FIG. 3.—Dehydration of rice grains over phosphorus pentoxide in the sorption tube.

A = Doddabyra. *B* = Mysore Kaddi. *C* = Doddabele. *D* = Coimbatore Sanna.

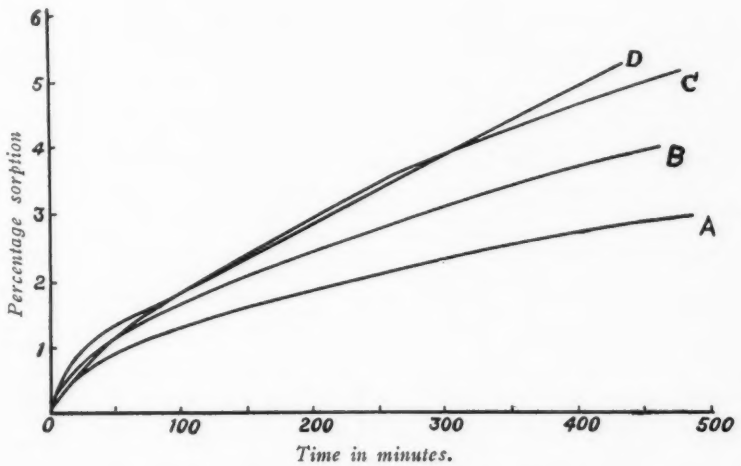

FIG. 4.—Sorption of water by dehydrated rice grains.

A = Doddabele. *B* = Doddabyra. *C* = Mysore Kaddi. *D* = Coimbatore Sanna.

TABLE C. *Desorption of water present in ' air-dry ' rice grains.*

1. *Desorption on evacuation.*

Period of evacuation	Percentage water remaining in the grains			
	Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
0 minutes	15·24%	10·03%	8·58%	9·36%
30 minutes ' Hyvac pump '	10·27	7·30	7·18	7·21
30 minutes ' Hg-vapour pump '	8·58	—	6·30	6·14
1 hour ' Hg-pump '	7·56	5·76	5·72	5·66
2 hours ' Hg-pump '	6·32	4·99	5·02	4·87
4 hours ' Hg-pump '	4·51	4·15	4·03	3·81

2. *Desorption over phosphorus pentoxide.*

Period of dehydration	Percentage water remaining in the grains			
	Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
0 minutes	4·51%	4·15%	4·03%	3·81%
30 minutes	4·29	3·98	3·85	3·63
60 minutes	4·06	3·80	3·68	3·45
90 minutes	3·95	3·62	3·50	3·34
2 hours	3·67	3·50	3·38	3·22
4 hours	3·05	3·10	2·76	2·80
6 hours	—	—	2·34	2·45
8 hours	2·05	2·51 ?	2·08	2·02
24 hours	0·51	0·89	0·70	0·54
34 hours	0·14	0·30	0·20	0·15
2 days	0·00	0·00	0·00	0·00

TABLE D. *Sorption of water by dehydrated rice grains at 40° C., in contact with water vapour saturated at 25° C.*

Period of sorption	Percentage sorption observed			
	Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
0 minutes	0·00%	0·00%	0·00%	0·00%
15 minutes	0·45	0·65	0·53	0·42
30 minutes	0·73	1·07	0·82	0·72
60 minutes	1·24	1·37	1·23	0·89
90 minutes	1·69	1·60	1·53	1·07
2 hours	2·09	1·92	1·87	1·43
3 hours	2·77	2·59	2·33	1·91
4 hours	3·44	3·32	2·66	2·15
6 hours	4·35	4·76	3·54	2·45
8 hours	5·31	6·00	—	3·04
12 hours	6·51	7·95	5·25	3·94
24 hours	7·22	9·02	6·54	5·36
36 hours	7·22	9·02	6·54	6·50
2 days	7·22	9·02	6·54	6·50

Sorption of water by rice grains at 28–30° C., in contact with water vapour saturated at 25° C.

Period of sorption	Percentage sorption observed			
	Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
0 minutes	7·22%	9·02%	6·54%	6·50%
1 hour	9·48	11·27	9·81	8·35
2 hours	10·16	12·70	11·09	9·55
4 hours	11·45	14·45	12·72	11·03
12 hours	13·85	17·09	—	—
24 hours	16·97	18·69	20·43	19·86
2 days	18·17	—	22·90	—

It is of interest to note that rice exhibits hysteresis in the sorption of water vapour. In experiments with Doddabyra rice, for instance, it was noticed that the dehydrated rice would take up 22·9 per cent. of water vapour at 29° C. at a corresponding pressure of nearly unity. On a second dehydration, however, the capacity for subsequent hydration markedly diminished and only 18·4 per cent. water was taken up. This closely corresponds to the observations by Fairbrother[7] on hysteresis effects in wheat starches. A more detailed investigation of this phenomenon is being undertaken in this laboratory.

(*d*) *Sorption of pyridine by rice.*—Pyridine sorption has been found by Sanjiva Rao and Seetharama Rao[8] to work well in the determination of soil colloids. The sorption of pyridine by 'air-dry' and 'dehydrated' rice grains was therefore tried. The 'air-dry' grains did not take up any pyridine but lost part of the water already present in them. Fully 'dehydrated' grains, however, showed a small and inappreciable sorption, less than 0·5 per cent. at 40° C.

Discussion.

The tabulated results show that varietal differences are exhibited by rice both during sorption and desorption of water vapour. Mysore Kaddi, Coimbatore Sanna and Nagpur Sanna which are recognised to be superior varieties, are dehydrated more readily than Doddabyra, Doddabele, Jeddu and Walya accepted as inferior in quality. The differences exhibited during sorption are more striking. The rate of hydration is much higher with the superior varieties. Studies in hydration have been found in general to be more satisfactory for determining quality of the rice than experiments in dehydration.

There is a marked difference in the behaviour of rice from freshly harvested paddy and rice of the same variety obtained from paddy that has been stored for some months. Rice from stored paddy is more easily dehydrated and gives a greater percentage of dehydration than rice from freshly harvested paddy. The change in physico-chemical behaviour on storage is significant in view of the well-known fact that on ageing paddy improves in quality.

The greater ease in dehydration as well as hydration exhibited by older samples of the same variety and by samples of superior varieties as distinguished from rices of poorer quality, indicates that in rice of good quality the capillaries are broader. Investigations on the gels of silicic acid and alumina carried out in this laboratory have shown that the size of capillaries affects the behaviour of gels in sorption of vapours. The effect of storage

on paddy seems to be to bring about a widening of the capillaries. Further work on this aspect of the problem is in progress.

These investigations were undertaken at the instance of the Agricultural Research Committee appointed by the Mysore Government. The authors wish to thank the Department of Agriculture—in particular Dr. V. K. Badami—for kind co-operation.

Summary.

Dehydration of different varieties of rice has been studied employing for dehydration a current of hot air or vacuum desiccation over phosphorus pentoxide.

Sorption and desorption of water vapour by rice under isothermal conditions has also been studied in a modified form of the quartz spring microbalance devised by McBain and Bakr.

It is found that superior varieties of rice lose water more readily during dehydration and take up water at a faster rate and to a greater extent than varieties of poorer quality.

Rice obtained from paddy that has aged is capable of easier hydration and dehydration than a sample of the same variety from freshly harvested paddy.

The investigations indicate that the capillaries in superior varieties of rice are broader than those in inferior kinds. Storage of paddy seems to cause a widening of these capillaries.

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PHYSICO-CHEMICAL INVESTIGATIONS ON VARIETAL DIFFERENCES IN RICE.

II. The Protective Action of Suspensions of Rice in Water.

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Introduction.

It is well known that there are marked differences in the protective powers of hydrophilic colloids. It was considered likely that there would be appreciable differences in the protective nature of the colloids in different varieties of rice. Gold numbers and Congo rubin numbers of suspensions from four varieties of rice (Mysore Kaddi, Coimbatore Sanna, Doddabyra and Doddabele, all harvested in 1933) were therefore determined.

Experimental.

Preparation of the rice powders.—The paddy was first dehusked by gentle rubbing between two asbestos cement plates. The grains thus released were ground in a mortar to completely pass through a 100-mesh sieve.

Preparation of the red gold sol.—Both the methods described by Zsigmondy[1,2] were tried. Satisfactory sols could not at all be prepared by his first method, though conductivity water and freshly distilled formaldehyde had been employed. The improved method of Zsigmondy involving the use of a nuclear sol gave good results but the procedure was rather tedious as the sol could only be prepared in small quantities at a time. The following procedure was therefore adopted in the preparation of the red sol.

To 500 c.c. of conductivity water heated to boiling in a clean resistance glass beaker was added 1·0 c.c. of a 1 per cent. solution of chlorauric acid ($HAuCl_4\ 3H_2O$) and this was followed immediately with one c.c. of ammonium hydroxide (2 Normal). The mixture was vigorously stirred, and the boiling continued till only a faint smell of ammonia remained. Formaldehyde (3–5 c.c. of a 0·4 per cent. solution) was then added. The mixture was stirred vigorously for two minutes and the heating discontinued. A deep red sol was formed almost immediately. This sol, when stored in Jena-glass bottles, retained its colour for about four weeks and then changed slowly to purple. It was quite satisfactory for gold number determinations as the colour transition from red to blue on addition of electrolytes (with or without protective colloids) was quite sharp. The sol however, was more dilute than the Zsigmondy sol.

Addition of ammonia to chlorauric acid gives better results than the use of sodium or potassium carbonate. Its use even in moderate excess does not affect the red sol formation. This is probably due to the fact that ammonia is a weak electrolyte. It is also probable that gold-ammonia complexes are formed which exert a stabilising influence on the red gold nucleii. Pauli[3] has reported that silver-ammonia complexes of the type $Ag(NH_3)_x$ stabilise silver sols.

For comparative purposes, the gold numbers of a few well-known hydrophilic colloids were determined, using this gold sol. The following procedure was adopted. 10·0 c.c. of the gold sol was mixed with a known volume of the protective colloid solution. The mixture was allowed to stand for 10 minutes. 1·0 c.c. of a 10 per cent. sodium chloride solution was added, the mixture shaken, and the colour change, if any, noted at the end of three minutes. As usual, the concentration which just prevented the colour change from red to blue, was taken to be the gold number. The results obtained are shown in Table A. For the sake of comparison, the accepted gold numbers with a Zsigmondy gold sol are also given.[4]

TABLE A.

Gold numbers of standard hydrophilic colloids with the new gold sol.

Name of the colloid	Gold number observed	Gold number accepted
Egg albumin ..	0·50 mgm.	0·10
Casein ..	0·04 mgm. (as calcium caseinate)	0·01 mgm. (as sodium caseinate)
Gelatin	0·02 mgm.	0·005–0·01 mgm.
Gum arabic (1st quality) ..	0·05 mgm.	0·15–0·25 mgm.

Gold numbers of rice starches.—1·0 per cent. suspension of the powdered rice in water was heated on the water-bath. At definite intervals samples were withdrawn, filtered and the protective value of the filtrates determined. The gold numbers were noticed to decrease as the time of heating of the suspension increased. Reproducible results however, could not at all be obtained and the method was therefore abandoned.

Congo rubin numbers of rice starches.—It is well known that starch is an efficient protective agent on Congo rubin solutions, being almost as good as gelatin.[5] As congo rubin is a substance with a definite composition and is spontaneously soluble in water, and as the quality of a gold sol is dependent on the method of preparation, it was felt that rubin numbers would be more satisfactory than gold numbers. Rubin numbers of rice suspensions were therefore determined.

A 1 per cent. suspension of rice powder was heated on the water-bath for a known interval of time, and filtered. A part of the suspension was also centrifuged for one hour. A known volume of the filtrate or centrifuged liquid was mixed with 1·0 c.c. of a 0·1 per cent. Congo rubin solution and allowed to stand. After 5 minutes it was mixed with 1·0 c.c. of a 2·5 normal potassium chloride solution, shaken well and the colour change observed at the end of 10 minutes. The volume of the filtrate which just prevented a change in the colour of the liquid was determined. This volume may be taken to be the rubin number of the rice. The values obtained are given in Table B. Congo rubin numbers of different varieties for suspensions of the same dilution are given in Table C.

TABLE B.

Congo rubin numbers of 1·0 *per cent. rice powder suspensions.*

Name of rice sample	Period of heating	Volume of starch solution to prevent colour change		
		Filtered	Centrifuged	Mean
Mysore Kaddi	2½ hours	10·5 c.c.	10·5 c.c.	10·5 c.c.
	5 hours	10·0	10·0	10·0
	19 hours	10·0	10·0	10·0
Coimbatore Sanna	2½ hours	10·5	10·0	10·3
	5 hours	10·5	10·0	10·3
	18 hours	10·5	10·0	10·3
Doddabyra	2½ hours	9·8	9·7	9·8
	4½ hours	9·5	9·5	9·5
	18 hours	9·5	9·5	9·5
Doddabele	3 hours	9·5	9·0	9·3
	5 hours	10·0	10·0	10·0
	18 hours	10·0	9·5	9·8

TABLE C.

Congo rubin numbers of 1 per cent. rice powder suspensions under identical dilution.

Name of the rice sample	Volume of filtrate to prevent colour change	Protective number under identical dilution
Mysore Kaddi ..	10·0 c.c.	9·6 c.c.
Coimbatore Sanna ..	10·5	10·5
Doddabyra	9·5	8·7
Doddabele	9·5	8·7

Influence of the time of heating.—To find out what influence the time of heating had on protective action, 1 per cent. suspensions of Mysore Kaddi rice were heated on the water-bath for different intervals of time and filtered, and the protective action of the filtrate was determined in each case. Congo rubin numbers were fairly constant after one hour's heating of the suspension. The results are given in Table D.

TABLE D.

Influence of the time of heating on the rubin number of 1 per cent. Kaddi rice suspension.

Period of heating	Volume of filtrate to prevent colour change	Period of heating	Volume of filtrate to prevent colour change
30 minutes	11·5 c.c.	2½ hours	11·0 c.c.
60	11·0	10	10·5
90	11·0	18	10·5
120	11·0		

Influence of concentration.—The influence of concentration on the rubin number of the suspensions was also determined. Doddabyra rice powder suspensions of concentrations varying from 1–5 per cent. were heated for 18 hours on the water-bath and filtered or centrifuged (filtration of

suspensions at and above 3 per cent. concentration was tedious and unsatisfactory) and the rubin numbers determined. No relationship could be established between concentration and the rubin number of the suspension. The results are given in Table E.

TABLE E.

Influence of concentration on the rubin numbers, at identical dilution of Doddabyra rice suspensions.

Concentration of suspension	Volume of liquid to prevent colour change		
	Filtered liquid	Centrifuged liquid	Mean
1 per cent.	12·0 c.c.	12·0 c.c.	12·0 c.c.
2	5·75	5·25	5·5
3	..	4·75–4·40	4·6
4	..	3·5	3·5
5	..	3·25	3·25

Discussion.

The experimental work recorded in this paper shows that the gold numbers of rice suspensions are not reproducible. The Congo rubin numbers are however, reproducible, but rice does not show any significant varietal differences in the rubin numbers. The two varieties of rice of superior quality appear to have smaller protective action than the inferior kinds.

The suspensions show practically the maximum protective action when kept at 96° C. for half an hour. Further heating for several hours causes only a slight diminution in the rubin numbers. It may be noted that the effect of heat on a rice suspension is similar to that of heat on the electrolytic conductivity as recorded in Part III of these studies. It may also be seen that the rubin number of the rice suspension is not directly proportional to the concentration.

Summary.

Gold numbers and Congo rubin numbers of rice suspensions have been determined. Use of ammonia in place of potassium carbonate gives more satisfactory results in the preparation of gold sols by Zsigmondy's method.

The gold numbers of rice suspensions are not reproducible. The Congo rubin numbers are reproducible but do not show significant variations between different varieties of rice. Thus varietal differences in rice cannot be correlated with any differences in protective action of the rice suspensions.

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PHYSICO-CHEMICAL INVESTIGATIONS ON VARIETAL DIFFERENCES IN RICE.

III. Electrical Conductivities of Rice Suspensions in Water.

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Introduction.

It has been established by Coehn, Grüzewska, Samec and others[1] that sols or suspensions of starch in water carry a negative charge. This charge has been attributed to amylopectin. Amylose has been found to be electrically neutral. Samec[1] has also noticed that the specific conductivity of a starch suspension increases on heating in an autoclave at 120° C. At the same time, the migration velocity in an electric field diminishes. There is a decrease in viscosity as well. He attributes these changes, which take place on continued heating, to the liberation of the electrolyte initially attached to the starch micelles. This work of Samec on the starches indicated the possibility of correlating quality of rice with conductivities of suspensions of rice in water. Conductivity measurements of such suspensions were therefore undertaken in this laboratory.

Experimental.

Four varieties of rice (Mysore Kaddi, Coimbatore Sanna, Doddabyra and Doddabele, all harvested in 1933) were employed in the experiments. A powdered sample from each, passing completely through a 100-mesh sieve, was prepared in the manner indicated in a previous paper (Part II). The measurements of conductivity were made in the usual manner with a circular type of wheatstone bridge and a telephone receiver. Conductivity water (sp. condy $= 1 \times 10^{-6}$ r. ohm at 30° C.) was employed in preparing the suspensions. Measurements of specific conductivity were made, at definite intervals of time, at four different temperatures 0° C., 30° C., 58° C. and 96° C. By adding thymol or toluene, the suspensions were protected from attack by micro-organisms.

Measurements were made at 0° C. by keeping the cell in a vacuum jar containing powdered ice in equilibrium with distilled water. The conductivity was very small to start with but slowly increased with time and did not become constant even after a week.

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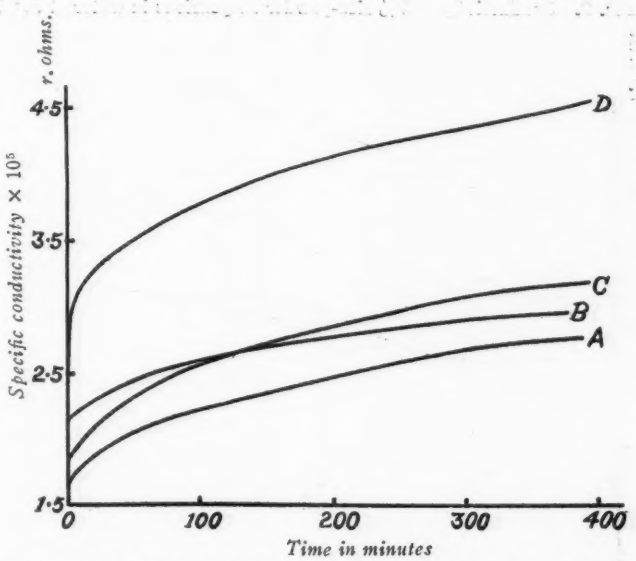
[1] M. Samec, *Trans. Far. Soc.*, 1935, **31**, 395 ; J. Alexander's *Colloid Chemistry*, **4**, 167.

An air-thermostat was employed for measurements at 30° C. The initial and the final conductivities, and the rate of increase of conductivity with time, were all higher than at 0° C. The increase was rapid at first and appreciably slowed down after about 10 hours. A fairly constant value was obtained after four days.

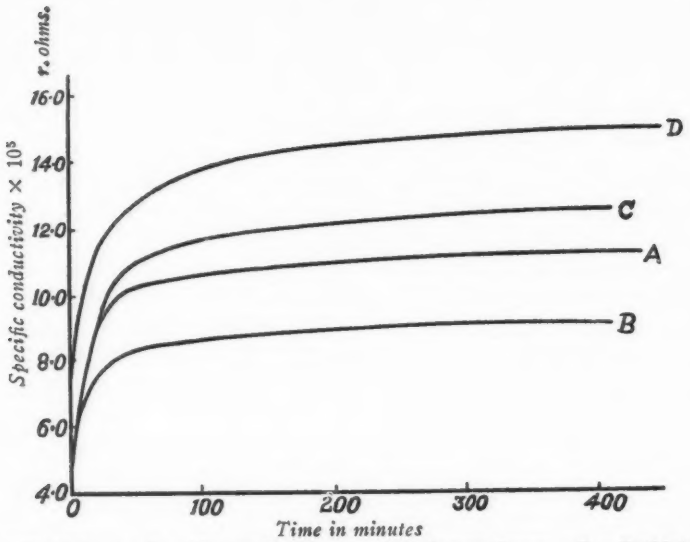
Effect of higher temperatures on the conductivity was studied by maintaining the suspensions at 58° C. or 96° C. in a water-bath. The actual conductivity determination however, was carried out at 30° C. (after cooling the hot suspension). The increase in conductivity with time was found to be high. At 58° C. constancy was attained in two days and at 96° C., in less than two hours. In the latter case however, a very small increase persisted even after heating for twenty-four hours. In all the experiments, the results were found to be reproducible. The results obtained are shown in Table A and Figs. 1–3.

Whole grains, in place of powders, were also used in the experiments at 58° C. and 96° C. The conductivity increase was very slow at 58° C. and constancy was not attained even after four days. But at 96° C., two days were found to be sufficient. Reproducibility of results however, was not



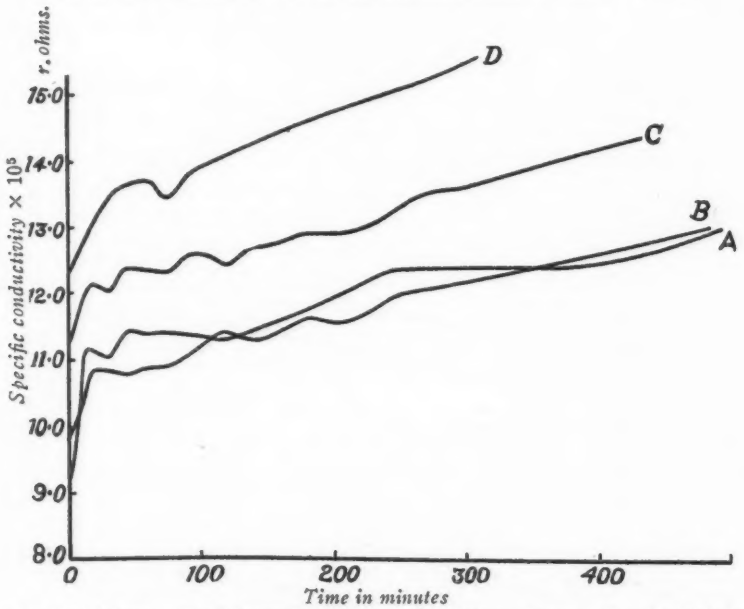
A = Doddabyra. *B* = Mysore Kaddi. *C* = Coimbatore Sanna. *D* = Doddabele.

FIG. 1. Conductivity of 1% rice-powder suspensions in water at 0° C.



A = Doddabyra. *B* = Mysore Kaddi. *C* = Coimbatore Sanna. *D* = Doddabale.

FIG. 2. Conductivity of 1% rice-powder suspensions in water at 30° C.



A = Doddabyra. *B* = Mysore Kaddi. *C* = Coimbatore Sanna. *D* = Doddabele.

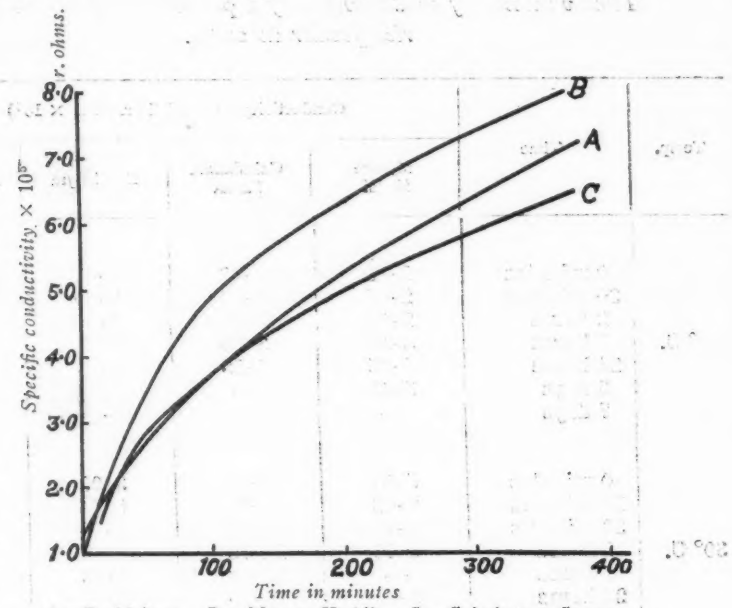
FIG. 3. Conductivity of rice-powder suspensions in water at 58° C.

TABLE A.

Time variation of conductivities of 1 *per cent. suspensions of rice powder in water.*

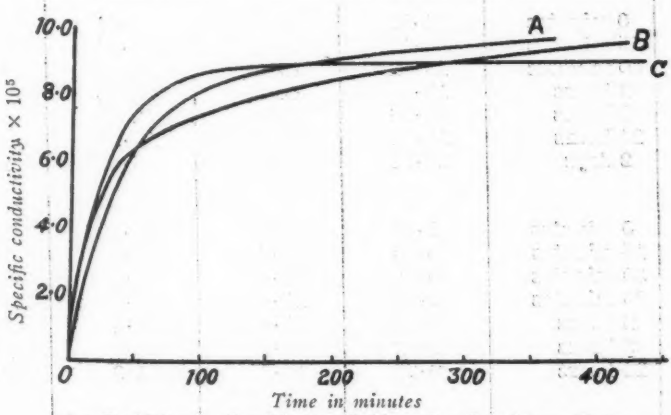
Temp.	Time	Conductivity observed (in r. ohms × 10^5)			
		Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
0° C.	0 minutes	2·12	1·83	1·64	2·59
	30 minutes	2·35	2·23	2·00	3·36
	2 hours	2·65	2·64	2·30	3·90
	8 hours	3·14	3·40	2·94	—
	24 hours	4·25	4·55	4·29	4·82
	3 days	5·42	—	5·68	6·72
	7 days	—	6·97	6·68	7·75
30° C.	0 minutes	5·04	4·76	3·98	5·98
	15 minutes	7·42	8·34	8·44	10·56
	30 minutes	8·18	10·20	9·71	12·22
	2 hours	8·70	11·75	10·75	14·00
	8 hours	—	12·70	11·32	15·15
	24 hours	9·84	13·79	11·98	17·99
	2 days	9·99	14·96	13·91	—
58° C.	0 minutes	11·27	9·75	9·14	12·30
	15 minutes	12·12	10·78	11·17	12·91
	60 minutes	12·31	10·91	11·35	13·72
	2 hours	12·42	11·45	11·40	14·00
	8 hours	14·36	12·96	12·89	14·78
	24 hours	17·22	15·81	15·58	20·54
	2 days	17·44	17·91	16·86	24·84
96° C.	0 minutes	9·46	12·3	11·2	13·7
	15 minutes	9·39	11·7	11·2	14·0
	30 minutes	9·58	11·8	11·2	14·1
	60 minutes	9·46	11·8	11·2	14·2
	2 hours	9·46	11·6	11·1	14·1
	8 hours	9·62	11·8	11·5	14·2
	24 hours	9·74	11·9	11·3	14·3

as high as with powdered rice. The results are shown in Table B and Figs. 4 and 5.



A = Doddabyra. *B* = Mysore Kaddi. *C* = Coimbatore Sanna.

FIG. 4. Conductivity of 1% rice grain suspensions in water at 58°C.



A = Doddabyra. *B* = Mysore Kaddi. *C* = Coimbatore Sanna.

FIG. 5. Conductivity of 1% rice grain suspensions in water at 96°C.

TABLE B.

Time variation of conductivities of 1 per cent. suspensions of rice grains in water.

Temp.	Time	Conductivity observed (in r. ohms × 10^5)			
		Mysore Kaddi	Coimbatore Sanna	Doddabyra	Doddabele
58° C.	0 minutes	0·99	0·87	1·14	0·96
	30 minutes	2·70	2·02	2·15	2·19
	60 minutes	3·75	2·93	2·87	2·83
	2 hours	5·27	4·03	4·04	4·04
	4 hours	6·87	5·38	5·70	5·70
	8 hours	8·30	6·98	7·85	7·55
	24 hours	10·54	8·82	10·10	9·78
	2 days	11·78	10·15	11·73	11·04
96° C.	0 minutes	1·79	1·47	1·15	1·27
	30 minutes	5·99	5·67	4·97	4·23
	60 minutes	8·17	6·86	7·24	6·95
	2 hours	8·85	7·88	9·10	9·28
	4 hours	9·25	8·96	9·36	10·22
	8 hours	9·62	10·24	10·26	11·18
	24 hours	9·84	10·86	11·24	11·77
	2 days	10·10	11·63	..	11·97

Discussion.

The results show that, in general, there is an increase in conductivity as the time of contact of the rice or rice powder with water increases. The increase is due to the liberation of electrolytes. There can be no appreciable liberation of electrolyte caused by hydrolysis of amylopectin, for the work

of Samec has shown that such hydrolysis is slow even at 120° C. in an autoclave. (The initial conductivity of a 2 per cent. suspension of pure potato starch was found by Samec to be about 2×10^{-5} r. ohms, and increased to about 8×10^{-5} r. ohms after it had been hydrolysed at 120° C. for 6–8 hours.) The curves however, show that the inferior varieties show a slightly higher specific conductivity than the superior ones, but the differences are not very significant.

The electrolytes responsible for the conductivity increase must therefore have been present in the rice in the free state, and were brought into solution as the water moved into the capillary spaces of rice. It is significant that while at 30° C. about four days were required for attainment of maximum conductivity, the corresponding time at 58° C. was two days and at 96° C. it was about half an hour. There is no doubt that at 96° C., owing to rapid hydration, the capillaries were quickly disintegrated and the electrolyte easily brought into solution.

The conductivity curve for 58° C. shows that there is a rapid initial increase, then a region of fluctuation and finally a slow increase in conductivity. The fluctuations seem to be due to the increase in viscosity, which tends to reduce the specific conductivity. The final conductivity of the suspension subjected to heat treatment at 96° C., was much less than the value for other temperatures owing to the fact that the suspension heated at 96° C. was markedly viscous on cooling to 30° C.—the temperature at which conductivities were measured.

Summmary.

The increase in conductivity with time of rice and rice powder suspensions in water has been studied at different temperatures. Varietal differences in the rates of increase have been observed, but they are not characteristic of quality. The increase in conductivity cannot be attributed to electrolytes liberated by hydrolysis of amylopectin as such hydrolysis is inappreciable, but is to be accounted for, by the dissolution of electrolytes already present in the free state in rice.

THE MECHANISM OF THE CLARIFICATION OF MUDDY WATER BY *STRYCHNOS POTATORUM* SEEDS.

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Introduction.

The *Strychnos potatorum* tree (also called the clearing nut tree) belongs to the *Strychnos* family and is found in many parts of India and Burma. The seeds are very hard and non-poisonous. They contain no strychnine, though Brucine is present. The seeds are still used in many rural parts of India for the clarification of muddy water. The use of albumin and casein in the refining of beer and wine is well known and it has been suggested[1] that the clarifying action in the present case is due to the albumin and casein present in the seeds. The mechanism of the clarification has been studied in this laboratory.

Experimental.

It was found that the seeds could be used in the investigation most conveniently in the form of a paste. They were first soaked in water for ten minutes and their outer coat rubbed off on a sand-stone. The seeds were then wiped dry with a filter paper and weighed (correct to a centigram). The paste used in each experiment was freshly made by rubbing the seeds on a sand-stone with small quantities of water.

The presence of alkaloids as cations in the paste was shown by the following experiment. The paste (25 c.c. of 2·5 per cent. concentration) was subjected to electrodialysis in an alundum thimble kept in an outer vessel containing distilled water. An e.m.f. of 150 volts was employed. The electrode in the thimble was of platinum while the other electrode, which surrounded the thimble, was of nickel gauze. The water in the outer vessel gave tests for alkaloid only when the gauze electrode was made the cathode.

The paste was almost neutral. Its pH as determined colorimetrically was 6·9 for a paste of 0·5 per cent. concentration and 6·8 for 5·0 per cent. strength. The protective action of the paste on a red gold sol was determined by Zsigmondy's method and found to be 2–2·5 times as high as that of egg albumin.

The clarifying action of the paste was studied on an aqueous suspension

of kaolin (about 1 per cent.), from which the coarser particles had been removed by sedimentation for a few days.

In a series of tall, graduated tubes of equal height (eudiometer tubes of 50 c.c. capacity) quantities of seed-paste varying from 0·01 c.c. to 25·0 c.c. were placed, and the kaolin suspension added to bring up the total volume to 50 c.c. The mixture was well stirred and allowed to stand for 3–4 days. At intervals the volume of clear water in each of the tubes was read off. In all the tubes, the boundary between the clear and the turbid water was noticed to be quite sharp. The results obtained are given in Table A and shown graphically in Figs. 1 and 2. The values indicate that for

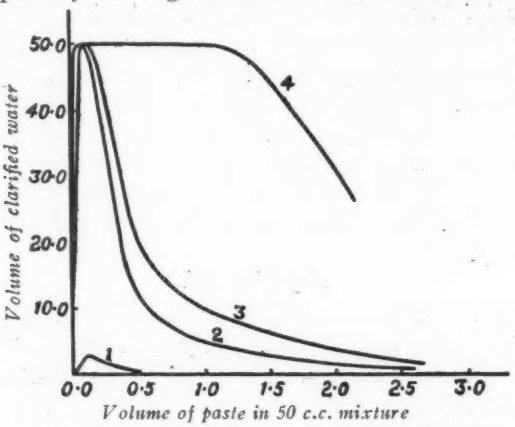

FIG. 1. Clarification of Kaolin suspension by 1·5% seed-paste.
Curves 1 = 3 hours ; 2 = 22 hours; 3 = 46; 4 = 96 hours.

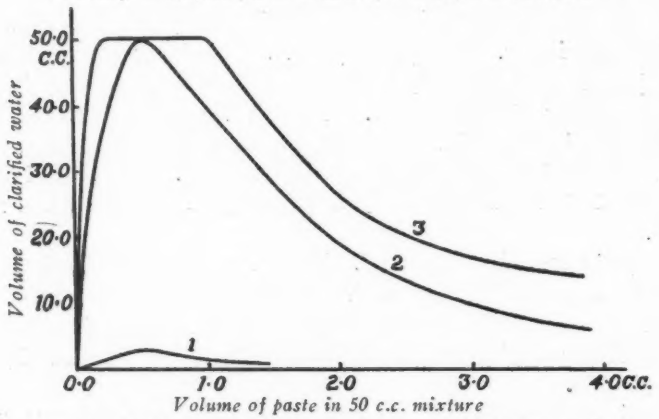

FIG. 2. Clarification of Kaolin suspension by 0·3 % seed-paste.
Curves 1 = 3 hours; 2 = 22 hours; 3 = 46 hours.

TABLE A.

Clarification of kaolin suspension in water by paste from Strychnos potatorum *seeds.*

Volume of paste in 50 c.c. mixture	1·5 % paste				0·3 % paste			0·06 % paste		
	Volume of clear water after				Volume of clear water after			Volume of clear water after		
	3 hours	22 hours	64 hours	96 hours	3 hours	22 hours	46 hours	3 hours	22 hours	46 hours
0·00 c.c. ..	0·2 c.c.	1·0 c.c.	2·0 c.c.	4·0 c.c.	0·2 c.c.	1·0 c.c.	2·0 c.c.	0·2 c.c.	1·0 c.c.	2·0 c.c.
0·01 ..	0·5	25	40	40	0·2	1·5	8·0*	..	..	..
0·05 ..	2·0	35	50	50	0·5	25	40	0·2	10	20
0·10 ..	2·5	50	50	50	1·0	25	50	0·5	15	35
0·50 ..	0·2	12	20	50	2·5	50	50	1·0	30	40
1·00 ..	0·1	5·0	10	40	1·5	40	50	1·5	30	50
2·5 ..	0·1	1·0	2·0	25	0·2	5·0	22	2·5	50	50
5·0 ..	0·0	0·5	1·0	20	0·1	5·0	12	1·5	40	50
10·0 ..	0·0	0·0	0·0	5·0	0·1	0·5	1·5	0·8	15	25
25·0 ..	0·0	0·0	0·0	0·0	0·0	0·1	0·2	0·1	7·0	15

clarification there is an optimum in the concentration (0·003 per cent.) of the seed material. About 24 hours were required for clarification, when the proper concentration was employed. It is of interest to note that the general practice in India is to allow nearly a day for water purification by this process. Excess of the paste actually stabilises the suspension.

To elucidate the mechanism of clarification, experiments were carried out on the kaolin suspension using in place of the seed-paste, the following :

(*a*) solutions of strychnine hydrochloride ;
(*b*) solutions of egg albumin and
(*c*) mixtures of (*a*) and (*b*) in varying proportions.

With strychnine hydrochloride (*a*) (Table B and Fig. 3) it was noticed that the volume of clear water showed a continuous increase with an increase

TABLE B.

Clarification of kaolin suspension in water by strychnine hydrochloride solution.

Volume of clarifying solution in 50 c.c. mixture	0·2% strychnine hydrochloride		0·4 % strychnine hydrochloride	
	Volume of clear water after		Volume of clear water after	
	23 hours	46 hours	23 hours	46 hours
0·00 c.c.	1·0 c.c.	2·0 c.c.	1·0 c.c.	2·0 c.c.
0·01	1·5	2·5	1·5	3·0
0·05	2·0	2·5	2·0	4·0
0·10	2·0	4·0	2·0	4·0
0·50	—	—	2·5	5·0
1·00	2·5	6·0	3·5	15·0
2·5	3·0	8·0	3·5	20·0
5·0	4·0	15	Complete clarification in 4 hours	
10·0	Complete clarification in 90 minutes		Complete clarification in 15 minutes	
25·0	Complete clarification in 10 minutes		Complete clarification in 5 minutes	

in the concentration of the alkaloid. The curves showed an initial small rise, then a range over which an increase in the concentration of the clarifying agent had relatively small effect and finally a third range over which the effect of concentration was very marked. With an increase in the time allowed for clarification, the second range became less pronounced.

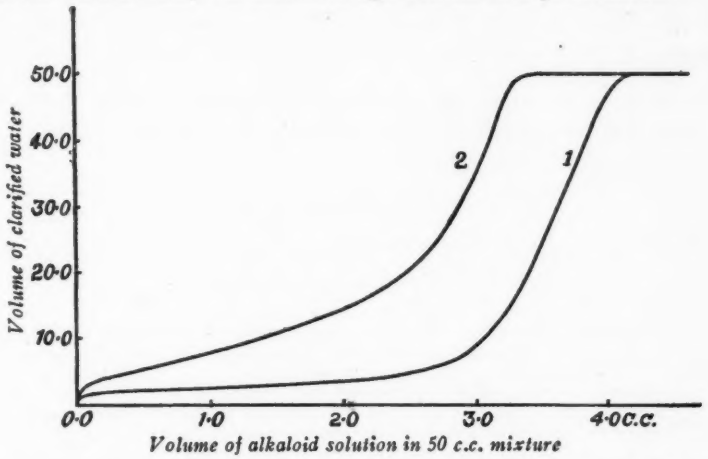

FIG. 3. Clarification of Kaolin suspension by 0·4 % Strychnine Hydrochloride solution. Curves 1 = 23 hours; 2 = 46 hours.

When egg albumin (*b*) was tried (Table C) it was found that there was no sedimentation at all but only a tendency towards greater stabilisation of the suspension.

TABLE C.

Clarification of kaolin suspension in water by 0·2 % *egg albumin solution.*

Volume of albumin solution in 50 c.c. mixture	Volume of clear water after	
	23 hours	46 hours
0·00 c.c.	1·0 c.c.	2·0 c.c.
0·01	1·5	2·5
0·05	1·5	3·0
0·10	1·5	3·0
0·50	1·5	3·0
1·0	1·5	3·0
2·5	1·5	3·0
5·0	1·5	3·0
10·0	1·0	2·5
25·0	1·0	1·5

In experiments (*c*) wherein mixtures of strychnine hydrochloride (0·2 per cent.) and egg albumin (0·1 per cent.) were employed (Table D, Fig. 4), the curve showed a steep rise, a maximum, then a fall and a final rise. The second rise was more pronounced when a longer time was allowed for clarification. On increasing the concentration of albumin (Fig. 5) the second rise disappeared, and the process of sedimentation showed a strong resemblance to that met with when the seed-paste is employed.

For comparative purposes experiments were carried out on the sedimentation of kaolin by barium chloride, with and without the addition of egg

TABLE D.

Clarification of kaolin suspension in water by a solution of strychnine hydrochloride containing egg albumin.

Volume of clarifying solution in 50 c.c. mixture	0·2 % strychnine hydrochloride solution with 0·1% albumin		0·2 % strychnine hydrochloride solution with 0·2% albumin		0·2% strychnine hydrochloride solution with 0·6% albumin	
	Volume of clear water after		Volume of clear water after		Volume of clear water after	
	21 hours	50 hours	21 hours	50 hours	21 hours	50 hours
0·00 c.c.	1·0 c.c.	5·0 c.c.	1·2 c.c.	2·1 c.c.	1·2 c.c.	2·1 c.c.
0·01	1·5	5·0	1·4	2·5	1·4	2·5
0·05	2·0	6·0	1·5	3·0	3·5	7·5
0·10	2·0	6·0	1·5	3·0	3·0	6·0
0·50	2·0	6·0	2·0	5·0	2·8	6·0
1·00	4·0	12·0	3·0	8·0	1·5	4·0
2·5	2·5	8·0	1·5	3·0	1·5	3·5
5·0	2·5	7·0	1·0	2·0	1·0	2·8
10·0	2·0	9·0	0·2	0·5	0·2	2·0
25·0	4·0	9·0	0·0	0·0	0·0	0·5

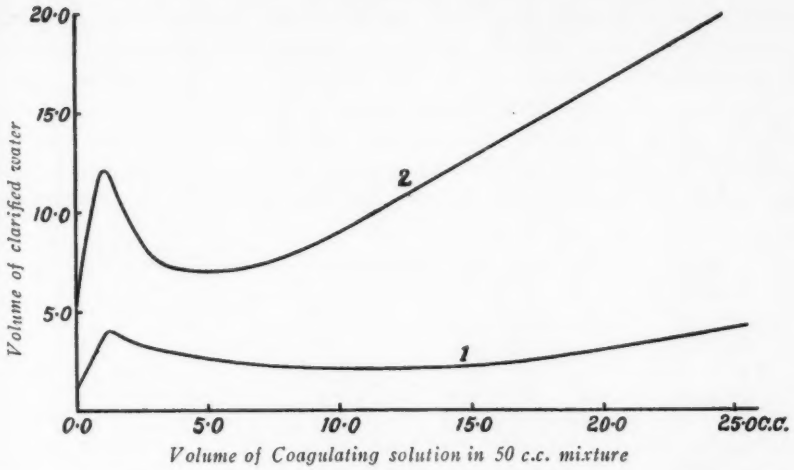

FIG. 4. Clarification of Kaolin suspension by 0·2 % Strychnine Hydrochloride solution containing 0·1 % egg albumin.

Curves 1 = 21 hours; 2 = 50 hours.

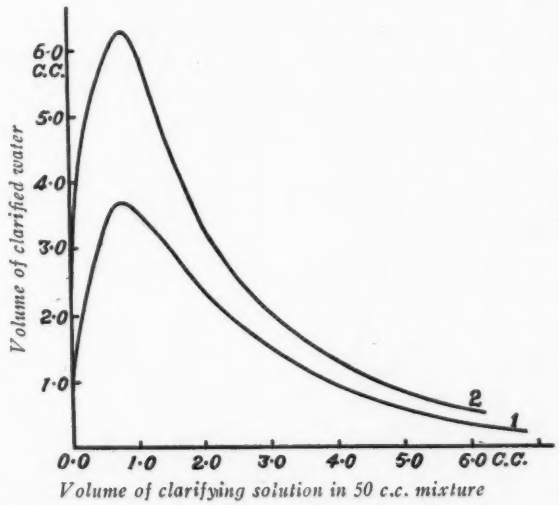

FIG. 5. Clarification of Kaolin suspension by 0·2 % Strychnine Hydrochloride solution containing 0·4 % egg albumin.

Curves 1 = 21 hours ; 2 = 50 hours.

albumin (Tables E and F, Figs. 6, 7 and 8). Barium chloride was selected because alkaloid ions resemble bivalent cations in coagulation processes.[2] The sedimentation effected by barium chloride showed a striking resemblance to that with strychnine hydrochloride (compare Figs. 3 and 6). The combined action of barium chloride and egg albumin resembled that of strychnine hydrochloride and albumin, or with the seed-paste alone (compare Figs. 1, 2 and 5 with Figs. 7 and 8). An attempt was made to study the

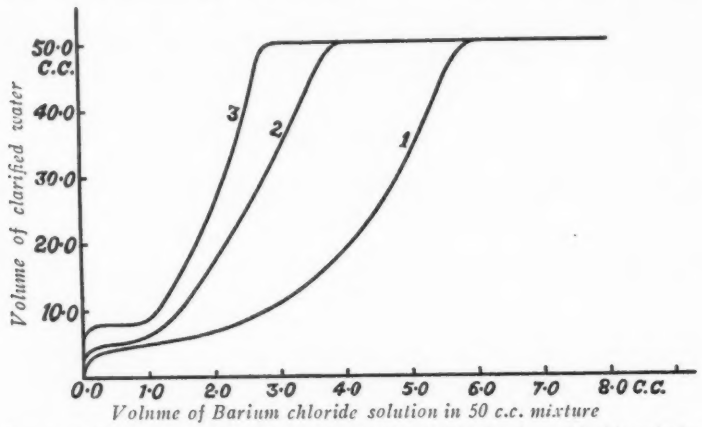

FIG. 6. Clarification of Kaolin suspension by 0·1 % Barium chloride solution.
Curves 1 = 24 hours ; 2 = 52 hours ; 3 = 96 hours.

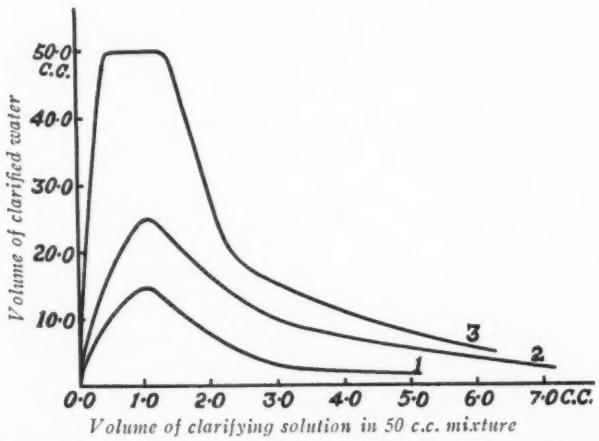

FIG. 7. Clarification of Kaolin suspension by 0·1 % Barium chloride solution containing 0·4 % egg albumin.
Curves 1 = 52 hours ; 2 = 72 hours ; 3 = 96 hours.

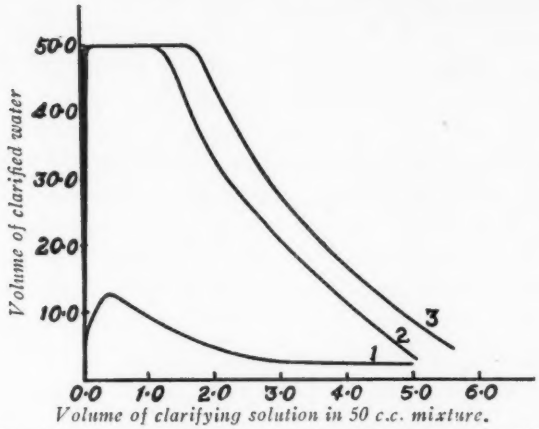

FIG. 8. Clarification of Kaolin suspension by 0·1 % Barium chloride solution containing 1·0 % egg albumin.
Curves 1 = 24 hours ; 2 = 52 hours ; 3 = 72 hours.

TABLE E.

Clarification of kaolin suspension in water by 0·1 % *barium chloride solution.*

Volume of barium chloride solution in 50 c.c. mixture	0·1% Barium chloride		
	Volume of clear water after		
	24 hours	52 hours	96 hours
0·00 c.c.	1·1 c.c.	2·0 c.c.	4·0 c.c.
0·01	1·5	3·0	4·5
0·05	2·5	4·0	6·5
0·10	3·0	4·0	6·0
0·50	4·0	4·5	7·0
1·00	5·0	6·0	9·0
2·5	8·0	25	40
5·0	25	50	50
10·0	Complete clarification in 12 hours		
25·0	Complete clarification in 30 minutes		

TABLE F.

Clarification of kaolin suspension in water by barium chloride solution containing egg albumin.

Volume of clarifying solution in 50 c.c. mixture	0·1% Barium chloride solution with 0·4% albumin			0·1% Barium chloride solution with 1·0% albumin		
	Volume of clear water after			Volume of clear water after		
	24 hours	52 hours	96 hours	24 hours	52 hours	96 hours
0·00 c.c.	1·1 c.c.	2·0 c.c.	4·0 c.c.	1·1 c.c.	2·0 c.c.	4·0 c.c.
0·01	1·5	2·5	6·0	—	—	—
0·05	4·0	5·0	14·0	5·0	25	50
0·10	5·0	6·0	18·0	8·0	50	50
0·50	2·5	6·0	50	12·0	50	50
1·0	2·5	15	50	9·0	50	50
2·5	2·0	4·0	18	3·0	25	50
5·0	2·0	2·0	8·0	2·0	3·0	25
10·0	0·0	0·0	1·0	0·0	0·0	15
25·0	0·0	0·5	0·5	0·0	0·0	1·0

sedimentation of kaolin with aluminium chloride in presence of albumin, but the process was complicated by the phenomenon of charge reversal.

The sedimentation of arsenious sulphide sol (0·05 per cent.) by the seed-paste was also tried. The results obtained were similar to those with kaolin (Table G). The curve showed a maximum only at an optimum concentration and not, as in the case of kaolin, over a concentration range. This was probably due to the fact that the arsenious sulphide sol was more unidisperse than the kaolin suspension.

Electrophoretic experiments showed the absence of charge reversal during the clarification. The paste carried a small negative charge. Mixtures of the paste and the arsenious sulphide sol (or kaolin) were also negatively charged at concentrations above and below the optimum.

TABLE G.

Clarification of 0·05% *arsenious sulphide sol by paste from* Strychnos potatorum *seeds.*

Volume of seed-paste in 50 c.c. mixture	1·5 % seed-paste					0·3% seed-paste				
	Volume of clear water after					Volume of clear water after				
	3 hours	24 hours	48 hours	72 hours	96 hours	3 hours	24 hours	48 hours	72 hours	96 hours
0·00 c.c. ..	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.	0·0 c.c.
0·01 ..	0·0	0·1	0·2	0·25	0·3	0·0	0 0	0·2	0·2	0·3
0·05 ..	0·0	0·2	0·3	0·4	0·5	0·0	0·2	0·3	0·4	0·8
0·10 ..	0·2	0·8	2·0	4·0	7·0	0·1	0·2	0·7	1·0	1·2
0·50 ..	0·1	0·2	0·4	0·6	0·8	0·5	1·0	1·4	1·6	2·0
1·0 ..	0·0	0·05	0·1	0·2	0·4	Complete clarification in 25 minutes				
2·5 ..	0·0	0·0	0·05	0·1	0·1	0·0	0·1	0·2	0·3	0·4
5·0 ..	0·0	0·0	0·0	0·0	0·05	0·0	0·05	0·15	0·2	0·3
10·0 ..	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·05	0·1	0·1
25·0 ..	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·05	0·1	0·1

Note :—Paste in 0·006 % concentration has maximum coagulating effect on the arsenious sulphide sol.

The method developed by Usher[3] for investigating rapid coagulation was found to be unsuitable for studying the clarification of arsenious sulphide or mastic sols as brought about by the paste.

Discussion.

The experimental results recorded in this paper indicate that clarification is due to the joint action of the colloids and the alkaloid present in the seeds. The albumin and other colloids present sensitise the suspension and the coagulation is then brought about by the alkaloid ions. The albuminous matter is not able, by itself, to clarify the water.

The seed-paste acts most efficiently when present in a certain optimum concentration. When larger quantities of paste are employed, though the concentration of the alkaloid ion increases no clarification takes place; for, the colloids present in the seed (which sensitise the suspension when present in small quantities) now actually stabilise it. This view is confirmed by the experiments with albumin in presence of strychnine hydrochloride or barium chloride.

Summary.

Clarification of muddy water by paste prepared from *Strychnos potatorum* seeds is due to the combined action of colloids and alkaloids present in the seeds. The albumin and other colloids sensitise the suspension and the coagulation is then caused by the alkaloid ions. The paste, if used in excess, fails to clarify the water. An optimum concentration of paste is therefore to be employed for efficient clarification.

Note.—Some preliminary work on this problem was carried out in this laboratory, under the direction of Prof. B. Sanjiva Rao, by K. N. Nagarkatte, I.C.S., who was obliged to terminate the investigation when he joined the Indian Civil Service.

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CORRELATION BY THE METHOD OF FACTORS.

By A. A. Krishnaswami Ayyangar.

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§ 1. Any correlation table which gives the frequencies (A_{pq}) for the simultaneous occurrence of paired values (p, q) of the variates (x, y) may be algebraically represented by the series :

$$f(x, y) \equiv \Sigma A_{pq} x^p y^q,$$

which may be called a correlation series if $\Sigma A_{pq} = 1$. This enables us to obtain simple formulæ for the mean, and the standard deviations of the x- and y-distributions and also the correlation between x and y. Further, as will be pointed out presently, if a correlation series can be factorised into other such series, we can express the statistical constants associated with the composite series in terms of those of the component series. Several known results are easily derived from this principle.

Adopting the usual notation for the constants $\bar{x}$, σ_x, p_{xy} (which represent the mean, standard deviation, product moment about the mean) we easily find :

$$\text{A} \begin{cases} \bar{x} = f_x{}_{x=y=1}, \ \bar{y} = f_y{}_{x=y=1}, \ \sigma_x^2 = \dfrac{\partial}{\partial x}\left(x \dfrac{\partial f}{\partial x}\right)_{x=y=1} - \bar{x}^2 = (f_{xx} + f_x - f_x{}^2)_{x=y=1} \\ \sigma_y^2 = (f_{yy} + f_y - f_y{}^2)_{x=y=1}, \ p_{xy} = \left(\dfrac{\partial^2 f}{\partial x \partial y}\right)_{x=y=1} - \bar{x}\bar{y} = (f_{xy} - f_x f_y)_{x=y=1} \end{cases}$$

Cor. : When $f(x, y)$ satisfies the differential equation $f_{xy} - f_x f_y = 0$, the coefficient of correlation is 0.

§ 2·1. *Lemma* : If $f(x, y) = \prod_{i=1}^{n} [f_i(x, y)]^{t_i}$, then

(i) $\dfrac{1}{f} \cdot f_x = \sum_1^n \dfrac{t_i}{f_i} f_{ix}$;

(ii) $\dfrac{1}{f} \cdot f_{xy} - \dfrac{1}{f^2} f_x \cdot f_y = \sum_1^n \left[\dfrac{t_i}{f_i} f_{ixy} - \dfrac{t_i}{f_i^2} f_{ix} \cdot f_{iy}\right]$;

(iii) $\dfrac{1}{f} \cdot f_{xx} - \dfrac{1}{f^2} f_x{}^2 = \sum_1^n t_i \left[\dfrac{1}{f_i} f_{ixx} - \dfrac{1}{f_i{}^2} f_{ix}{}^2\right]$.

These results follow readily from logarithmic partial differentiation.

§ 2·2. If the functions are all correlation series the f's become all equal to 1, when $x = 1 = y$ and we have, from (A) and the above lemma :

(1) $\bar{x} = \Sigma t_i \bar{x}_i, \quad \bar{y} = \Sigma t_i \bar{y}_i$

(2) $\sigma_x^2 = \Sigma t_i \sigma_{xi}^2, \quad \sigma_y^2 = \Sigma t_i \sigma_{yi}^2$

(3) $p_{xy} = \Sigma t_i p_{xyi}$; where

$\bar{x}_i, \bar{y}_i, \sigma_{xi}, \sigma_{yi}, p_{xyi}$ refer to the series $f_i(x, y)$ and the corresponding symbols without the i-subscripts refer to $f(x, y)$. If γ_i be the coefficient of correlation associated with $f_i(x, y)$, since $p_{xyi} = \gamma_i \sigma_{xi}, \sigma_{yi}$, we have the following theorem which expresses the correlation associated with a series in terms of those of its factors.

THEOREM : If $\sigma_{xi}, \sigma_{yi}, \gamma_i$ be the standard deviations and the coefficient of correlation associated with the series $f_i(x, y)$, then the coefficient of correlation associated with the function $\prod_{i=1}^{n} \{f_i(x, y)\}^{t_i}$ is

$$\sum_1^n t_i \gamma_i \sigma_{xi} \sigma_{yi} \Big/ \sqrt{\sum_1^n t_i \sigma^2_{xi} \cdot \sum_1^n t_i \sigma^2_{yi}}$$

Cor. : The correlation coefficient is invariant when t_i is changed to kt_i $(i = 1, 2, \cdots n)$, *i.e.*, $f(x, y)$ and $\{f(x, y)\}^k$ have the same correlation.

§ 3. The results given above have several applications to well-known data. We will be content with pointing out a few.

(i) Let $f(x, y) \equiv P + Qx$ where $P + Q = 1$.

Here $\bar{x} = Q, \sigma_x^2 = Q - Q^2 = PQ, \sigma_y^2 = 0$; hence for the binomial distribution $(P + Qx)^n$, the mean and the standard deviations are respectively nQ and $\sqrt{nPQ}$.

(ii) Let $f_1(x, y) \equiv Q + Px$, $f_2(x, y) \equiv Q + Py$, and $f_3(x, y) \equiv Q + Pxy$, where $P + Q = 1$.

Then $\bar{x}_1 = P, \ \bar{y}_1 = 0, \ \sigma_{x_1}^2 = PQ, \ \sigma_{y_1}^2 = 0, \ \gamma_1 = 0$;

$\bar{x}_2 = 0, \ \bar{y}_2 = P, \ \sigma_{x_2}^2 = 0, \ \sigma_{y_2}^2 = PQ, \ \gamma_2 = 0$;

$\bar{x}_3 = P, \ \bar{y}_3 = P, \ \sigma_{x_3}^2 = PQ, \ \sigma_{y_3}^2 = PQ, \ \gamma_3 = 1.$

Hence, for the function

$(Q + Px)^{t_1} (Q + Py)^{t_2} (Q + Pxy)^{t_3}$, we have

$\bar{x} = P(t_1 + t_3), \quad \bar{y} = P(t_2 + t_3), \quad \sigma_x^2 = (t_1 + t_3)PQ,$

$\sigma_y^2 = (t_2 + t_3)PQ, \quad \gamma = t_3 / \sqrt{(t_1 + t_3)(t_2 + t_3)}$

In particular, if $t_1 = t_2$, then $\gamma = t_3/(t_1 + t_3)$.

These results have an important significance and are related to the following theorem :—

*Given an infinite number of balls in the ratio P white to Q black ($P + Q = 1$) and pairs of drawings are made thus: In the first draw, there shall be n_1 balls and in the second n_2; but before the second draw select at random n_3 balls from the first group and count them also in the second group, so that for the second group there shall be only $(n_2 - n_3)$ balls to be drawn from the infinite number. Then, the correlation between the number of white balls in the two groups is $n_3/\sqrt{n_1 n_2}$, which reduces to n_3/n_1 when $n_1 = n_2$.

For, the probability that there are p white balls in the first group, and q in the second is clearly

$$\sum_{r=0} {}^{n_1-n_3}C_{p-r}\, P^{p-r}\, Q^{n_1-n_3-p+r}.\ {}^{n_2-n_3}C_{q-r}\, P^{q-r}\, Q^{n_2-n_3-q+r}.\ {}^{n_3}C_{r}\, P^{r}\, Q^{n_3-r}$$

the summation to extend up to the least of the numbers p, q and n_3, which is the coefficient of $x^p y^q$ in

$$(Q + Px)^{n_1-n_3}\ (Q + Py)^{n_2-n_3}\ (Q + Pxy)^{n_3}.$$

This function therefore represents the correlation series of the problem.

Applying our results, we readily verify the given correlations. An analogous problem of coins leads to the same correlation coefficient, when n_1 coins and n_2 coins are thrown successively and the heads in these throws are correlated under the circumstance that in the second throw n_3 coins are left as they were in the first throw.

The results of these problems are important in that they illustrate a general property of the Pearson Coefficient of correlation, *viz.*, that its square is equal to the product of the ratios of the common elements to the total number that enter into the structure of the two variates in a certain special manner such that they may be regarded as the arithmetical sum of uncorrelated elements of equal variability.†

We conclude with the remark that we are now in a position to frame a correlation table of any degree of complexity having a given coefficient of correlation, and conversely, if we can factorise the series derived from a correlation table, we can simplify our work if the factors have known correlations and standard deviations. For frequencies derived from observations, the process outlined here has evidently no application.

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* For a different proof of an allied result *vide* Camp, *The Mathematical Part of Elementary Statistics*, p. 293, where a reference is given to *Annals of Mathematics*, Series 2, 21, pp. 306-332.

† *Vide* p. 120, *Methods of Correlation Analysis*, by Ezekiel (John Wiley & Sons, 1930).

AN EXPLANATION OF THE MAXIMUM IN SECONDARY ELECTRON EMISSION FROM METALS.

By D. R. Bhawalkar, M.Sc., Ph.D.
(Communicated by Prof. K. S. Krishnan, D.Sc.)

When a beam of electrons of energy ' V ' volts bombards a metallic target a fraction of its energy is used in heating the target and excite radiations while the rest appears in exciting secondary electrons.[1] Considerable work has been done on the excitation of secondary electrons from metals.[2,3,4] The general nature of the secondary electron emission curves[5] is shown in Fig. 1. If ' I_s ' denotes the total secondary electrons, ' I_p ' the total primary electrons and ' V ' the energy in volts of the bombarding electrons, the curve plotted for ' I_s/I_p ' against ' V ' increases with ' V ' and attains a flat maximum at about a few hundred volts and slowly falls down for higher values of ' V '. (As a secondary structure the curve shows ' breaks ' which correspond to the ' breaks ' observed in the total intensity of the soft X-rays excited from the same metal.) The value of ' V ' corresponding to the maximum is characteristic of the metal provided it is thoroughly degassed, and the purpose of the present paper is to give an explanation of the occurrence of this maximum in the secondary electron emission curves.

The exact nature of the mechanism of secondary electron emission is still obscure, though some of the experimental facts, especially those corresponding to lower values of ' V ', have been to some extent explained.[6] The existence of the maximum indicates that some process reverse to secondary electron emission must be going on within the metal target. The primary electrons penetrate deeper as their energy increases and consequently the corresponding secondary electrons are also generated deeper within the metal. The secondary electrons as a rule have small energies (of the order of a few volts only) and will be absorbed in trying to emerge out of the target. This at once explains the presence of the maximum in the above curve. The flat nature of the maximum can also be understood as the secondary electrons are generated not at one particular point but all along the path of the primary electrons in the metal.

This hypothesis can be verified roughly from the existing experimental data. According to Thomson–Whiddington Law[7] the energy of a primary beam of electrons decreases according to the following relation :

$$V_x^2 = V^2 - a.x. \qquad (1)$$

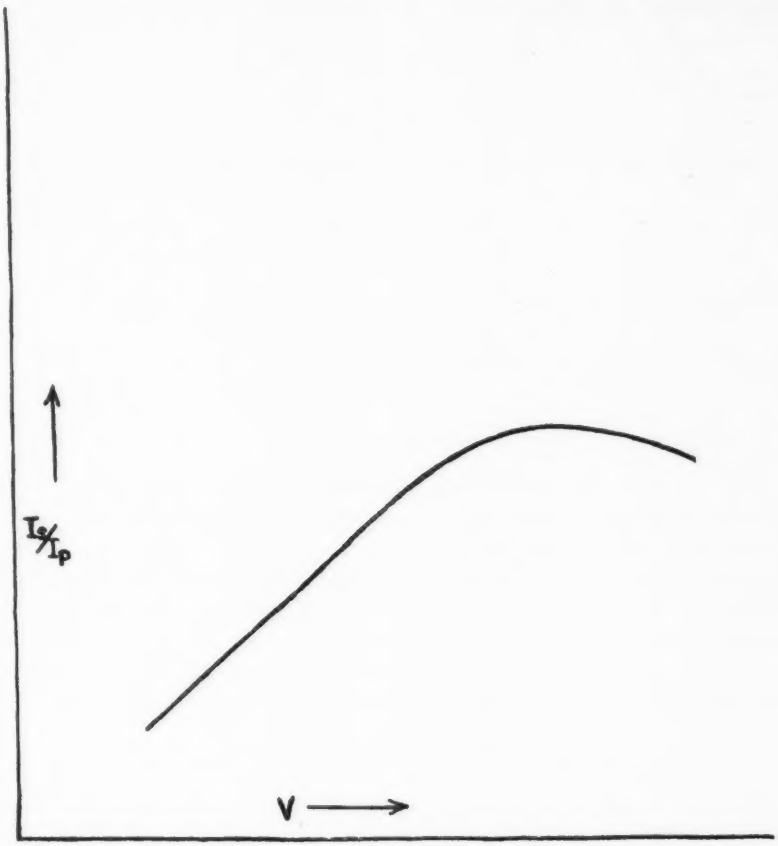

FIG. 1.

where ' V ' is the energy of the primary electrons, ' V_x ' is the energy after traversing a distance ' x ' in the metal and ' a ' is a constant depending on the metal of the target. The number of secondary electrons ' δI_s' generated by the primary electrons of energy ' V ' in a distance ' δx ' within the target will be proportional to the number of primaries ' I_p ' and to the energy lost in the distance ' δx '. Thus,

$$\delta I_s = K_1 I_p \frac{\delta V}{\delta x} \delta x \qquad (2)$$

Of these secondaries only a fraction will be able to come out of the target. If ' a ' is the coefficient of absorption, the number of secondary

electrons that will actually leave the target will be :

$$\delta I_s = K_1 I_p \frac{\delta V}{\delta x} \delta x . e^{-a\delta x}$$

$$= K_1 I_p \frac{\delta V}{\delta x} \delta x (1 - a\delta x) \quad (3)$$

Intergrating equation (3) the total number of secondary electrons will be

$$I_s = K_1 I_p (V - aV \int_0^{x_{max}} \delta x) \quad (4)$$

The value of x_{max} is $\frac{V^2}{a}$, from equation (1)

$$\therefore \quad I_s = K_1 I_p V \left(1 - a\frac{V^2}{a}\right)$$

$$\therefore \quad I_s/I_p = K_1 V \left(1 - \frac{a}{a} V^2\right) \quad (5)$$

' a ' is known to be of the order of 10^{11} and ' a ' of the order of 10^5. Thus the second term in the right-hand side of equation (5) is negligible for small values of ' V ' and the relation between ' I_s/I_p ' and ' V ' would be more or less linear as has been experimentally observed. The second term becomes of importance as ' V ' increases and the curve should flatten for sufficiently high values of ' V '. The maximum value of ' I_s/I_p ' will correspond to the voltage obtained by differentiating and equating to zero the right hand side of equation (5). This value of ' V ' is given by

$$V_1 = \sqrt{\frac{K_1 a}{3a}} = k\, a^{\frac{1}{2}} \quad (6)$$

It is well known from the experiments of Whiddington and also of Terrill[8] that ' a ' varies as the density ' ρ ' of the target. Thus the value of the energy of the primary electrons which corresponds to the flat maximum in the secondary electron curve should vary as the square-root of the density of the target. The accompanying figure shows the relation between ' $\rho^{\frac{1}{2}}$ ' and the value of ' V ' corresponding to the flat maximum taken from the existing data.[9] It must be pointed out that the maximum is flat and as such the value of the corresponding voltage can be determined only approximately. As ' a ' is of the order of 10^{11} and ' a ' of the order of 10^5, this value of the voltage ' V_1' comes out to be of the order[10] of 1000 from the last equation, which is of the order experimentally observed. Thus the general characteristics of the secondary electron emission can be satisfactorily explained by the assumption of absorption of the secondary electrons within the target.

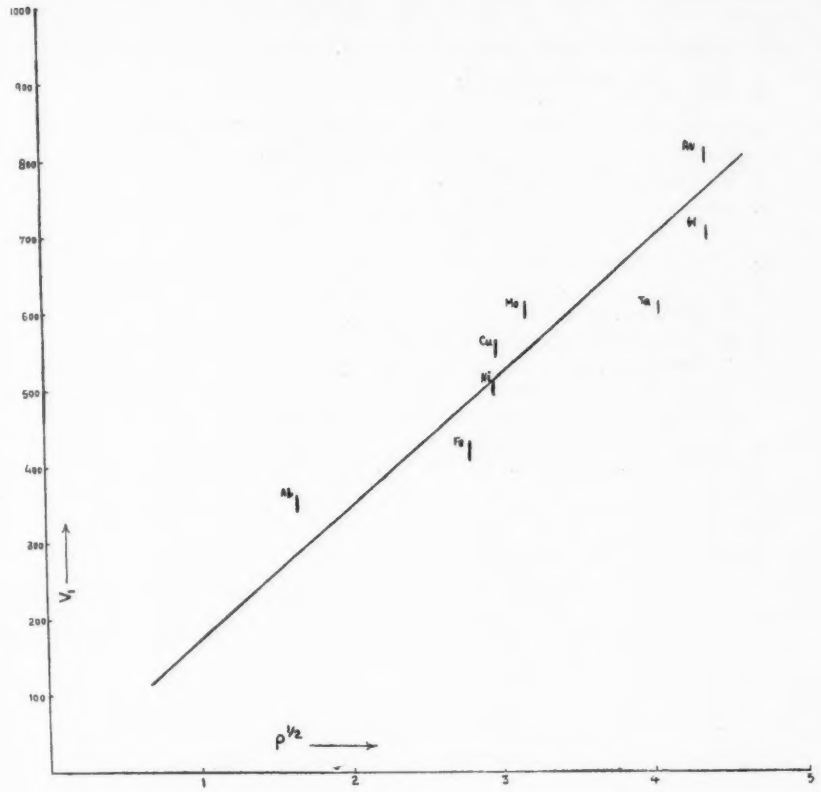

FIG. 2.

Summary.

It is well known that the curve plotted for 'I_s/I_p : V', where 'I_s' is the total secondary electrons corresponding to the primary electrons 'I_p' of energy 'V' volts, shows a flat maximum at higher values of 'V'. The presence of this maximum is explained on the assumption that the rate of loss of energy of the primary electrons obeys the Thomson–Whiddington Law and the secondary electrons generated at various depths are absorbed by the target on their way out. The relation derived on this assumption shows the dependence of the value of the voltage, corresponding to this maximum, on the density of the metal as has been observed experimentally.

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AULUCK'S GENERALIZATION OF THE SIMSON LINE PROPERTY.[1]

By S. Chowla.

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1. Let $l_m \equiv p_m - x\cos\alpha_m - y\sin\alpha_m = 0$ $(1 \leqslant m \leqslant 5)$ be the equations of 5 lines in a plane. The foot of the perpendicular from (x, y) on $l_m = 0$ is the point $x + l_m\cos\alpha_m$, $y + l_m\sin\alpha_m$. Hence the point (x, y) lies on the conic which passes through the feet of the perpendiculars from (x, y) on the five lines if the sixth order determinant

$$\begin{vmatrix} x^2 & xy & y^2 & x & y & 1 \\ (x + l_1\cos\alpha_1)^2 & \cdot & \cdot & \cdot & y + l_1\sin\alpha_1 & 1 \\ & \cdot & \cdot & \cdot & & \\ (x + l_5\cos\alpha_5)^2 & \cdot & \cdot & \cdot & y + l_5\sin\alpha_5 & 1 \end{vmatrix} = 0$$

which immediately reduces to the 5th order determinant

$$l_1l_2l_3l_4l_5 \times \begin{vmatrix} l_1\cos^2\alpha_1 & l_1\cos\alpha_1\sin\alpha_1 & l_1\sin^2\alpha_1 & \cos\alpha_1 & \sin\alpha_1 \\ & \cdot & \cdot & \cdot & \\ l_5\cos^2\alpha_5 & l_5\cos\alpha_5\sin\alpha_5 & l_5\sin^2\alpha_5 & \cos\alpha_5 & \sin\alpha_5 \end{vmatrix} = 0$$

or, by addition of the 3rd column, x times the 4th column and y times the 5th column to the first column,

$$l_1l_2l_3l_4l_5 \begin{vmatrix} p_1 & l_1\cos\alpha_1\sin\alpha_1 & l_1\sin^2\alpha_1 & \cos\alpha_1 & \sin\alpha_1 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ p_5 & l_5\cos\alpha_5\sin\alpha_5 & l_5\sin^2\alpha_5 & \cos\alpha_5 & \sin\alpha_5 \end{vmatrix} = 0,$$

a seventh degree curve consisting of the 5 lines themselves and a conic. Let M_1 be the Miquel point of the lines $l_m = 0$ $(2 \leqslant m \leqslant 5)$, etc. We show that this conic passes through $M_1, \cdots, M_5$ and hence the conic is a circle. Since M_1 is the focus of the parabola touching the lines $l_m = 0$ $(2 \leqslant m \leqslant 5)$, the feet of the perpendiculars from M_1 lie on a straight line (directrix of the

[1] This note contains a slight change in the proof of Auluck's theorem I below (he omits the proof of the clause that the locus which is the subject of Theorem I, also consists of the 5 lines themselves). We also give two additional theorems (II and III).

parabola). Hence M_1 has the property that the 5 feet of the perpendicualrs from it on the 5 lines $l_m = 0$ lie on a conic (which degenerates into a pair of straight lines) through it. Hence

THEOREM I. *Given 5 lines in a plane, the locus of a point with the property that the feet of the perpendiculars from this point on the 5 lines lie on a conic through the point itself, is a 7th degree curve consisting of the 5 lines themselves and the circle which passes through the 5 Miquel points of the lines taken 4 at a time.*

2. From this and the sequence of Miquel's theorems we easily obtain

THEOREM II. *Given 6 lines in a plane, there are in general at most 13 points with the property that the feet of the perpendiculars on the 6 lines from any of these points lie on a conic passing through the point from which the perpendiculars are dropped. These 13 points are*

(i) *The Miquel Point associated with the 6 lines.*

(ii) *The points (12 in all) where each of the lines meets the Miquel circle associated with the other 5 lines.*

3. The method used to prove Theorem I generalizes to prove (theorem I is the case $n = 2$).

THEOREM III. *The locus of a point which moves so that the feet of the perpendiculars from this point on to* $\left(\frac{n^2+3n}{2}\right)$ *hyper-planes (in space of n dimensions) is a hyper-quadric passing through the point itself, is a hyper-surface of degree* $\frac{n^2+3n}{2} + \frac{(n-1)(n+2)}{2}$ *consisting of the* $\frac{n^2+3n}{2}$ *hyper-planes and a hyper-surface of degree* $\frac{(n-1)(n+2)}{2}$.

THE REPRESENTATION OF A LARGE NUMBER AS A SUM OF "ALMOST EQUAL" SQUARES.

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1. Wright has announced that[1]

Theorem I. *Every positive integer* $N \not\equiv 0 \pmod 8$ *is expressible in the form*

$$N = m_1^2 + m_2^2 + m_3^2 + m_4^2 \tag{1}$$

where the m's *are integers satisfying*

$$\frac{N}{4} - m_i^2 = O(N^{\frac{5}{6}}) \quad [1 \leqslant i \leqslant 4]$$

and he has proved (*loc. cit.*) that this result is true with

$$\frac{N}{4} - m_i^2 = 0\,(N).$$

By an entirely elementary method we prove the sharper

Theorem II. *If* $N \not\equiv 0 \pmod 8$, *then* (1) *is true with*

$$\frac{N}{4} - m_i^2 = O\,(N^{\frac{2}{3}}) \quad [i = 1, 2, 3, 4]. \tag{2}$$

Proof.

Case I. $N \equiv 2$ or $6 \pmod 8$

Write

$$N - 4m^2 = P \tag{3}$$

where $4m^2$ is the nearest even perfect square below N. Then $P \equiv 2, 6 \pmod 8$. Hence

$$P = x_1^2 + x_2^2 + x_3^2 \tag{4}$$

where $x_1 + x_2 + x_3 \equiv 0 \pmod 2$. Hence we can write

$$x_1 = a + b,\ x_2 = b + c,\ x_3 = c + a \tag{5}$$

where a, b, c are integers. From (3), (4), (5),

$$N = (m + a)^2 + (m + b)^2 + (m + c)^2 + (m - a - b - c)^2 \tag{6}$$

where, since

$$P = O\,(N^{\frac{1}{2}}) \tag{7}$$

[1] This is a special case of his result in *Q. J. M.* (Oxford), 1936. Tchudakoff has recently proved a similar result for cubes.

we have from (4) and (5),

$$a, b, c = O(N^{\frac{1}{4}}) \tag{8}$$

Hence

$$\begin{aligned}(m+a)^2 &= m^2 + 2ma + a^2 \\ &= \frac{N}{4} + O(\sqrt{N}) + O(N^{\frac{3}{4}}) + O(N^{\frac{1}{2}}) \\ &= \frac{N}{4} + O(N^{\frac{3}{4}}),\end{aligned} \tag{9}$$

and the same is true of $(m+b)^2$, $(m+c)^2$, $(m-a-b-c)^2$. Thus Theorem II is proved in Case I [from (6) and (9)].

Case II. $N \equiv 1 \pmod 2$.

Let $4m^2 - 2m$ be the nearest integer of this form below N. Put

$$N - 4m^2 + 2m = P \tag{10}$$

so that $P \equiv 1 \pmod 2$ and $4P - 1 \equiv 3 \pmod 8$.

Hence

$$4P - 1 = x_1^2 + x_2^2 + x_3^2 \tag{11}$$

where x_1, x_2, x_3 are all odd and can therefore be chosen so that (*by changing all their signs if necessary*)

$$x_1 + x_2 + x_3 \equiv 1 \pmod 4 \tag{12}$$

If we put

$$x_1 = 2b + 2c - 1, \quad x_2 = 2c + 2a - 1, \quad x_3 = 2a + 2b - 1 \tag{13}$$

it follows from (12) and (13) that a, b, c are all integers. From (11) and (13),

$$\begin{aligned}4P - 1 = 8(a^2 + b^2 + c^2 + ab + bc + ca) \\ - 8(a + b + c) + 3.\end{aligned} \tag{14}$$

or

$$\begin{aligned}P = 2(a^2 + b^2 + c^2 + ab + bc + ca) \\ - 2(a + b + c) + 1.\end{aligned} \tag{15}$$

From (10) and (15),

$$\begin{aligned}N = (m-a)^2 + (m-b)^2 + (m-c)^2 \\ + (m + a + b + c - 1)^2\end{aligned} \tag{16}$$

Since a, b, c are $O(N^{\frac{1}{4}})$ the rest of the proof proceeds as in Case I.

Case III. $N \equiv 4 \pmod 8$.

This follows from Case II by multiplication by 4. Theorem II is now completely proved.

Note added 10–7–37.

Wright's proof of Theorem I has appeared in *Proc. London Math. Soc.*, **42** (1937), 481–500. The error term is improved to $O(N^{\frac{4}{5}+\epsilon})$ for any positive ϵ. Our index is slightly better.

ON THE THEORY OF NON-LINEAR INTEGRAL EQUATIONS.

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Received April 19, 1937.

1. *Introduction.*

The object of this paper is to study the infinite system of non-linear integral equations :

$$u_n(x) = f_n(x) + \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y)\, u_k(y)\, u_l(y)\, dy,$$
$$(n = 1, 2, \cdots \infty).$$

The sum is always taken from 1 to ∞ throughout this paper.

The method of successive approximations is employed to obtain a solution of this system. But when we proceed to establish the convergence and uniqueness of these approximations, we find that two cases arise according to the nature of the conditions which the given functions f_n, g_n, h_n satisfy.

In the first case, where

$$\sum_n |f_n(x)| = c, \quad |g_n(x, y)| \leqslant b, \quad \sum_n |h_n(k, l; x)| \leqslant a,$$

the solution exists only when x lies in a certain restricted domain. But if the last two conditions are replaced by the relation

$$\sum_n \left| \int_0^x g_n(x, y)\, h_n(k, l; y)\, dy \right| \leqslant a,$$

we find that the solution of the system of integral equations exists for all x however large.

These integral equations have a fundamental importance in the theory of partial differential equations of hyperbolic and parabolic type. Particular cases have been considered by the writer in several papers published recently.*

* M. R. Siddiqi, (1) "Zur Theorie der nicht-linearen partiellen Differentialgleichungen vom parabolischen Typus.," *Math. Zeitschr.*, 1932, **35**, 404; (2) "On a system of non-linear partial differential equations," *Journal, Osmania Uni.*, 1935, **3**, 1; (3) "Cauchy's Problem in a non-linear partial differential equation of hyperbolic type," *Proc. Camb. Phil. Soc.*, 1935, **31**, 195; (4) "On the theory of non-linear differential equations of parabolic type II," *Math. Zeitschr.*, 1935, **40**, 484.

2. Solution in the Restricted Domain.

We wish to determine a solution of the system of non-linear integral equations :

$$(1) \qquad u_n(x) = f_n(x) + \int_0^x g_n(x, y) \sum_{k, l} h_n(k, l ; y) u_k(y)\, u_l(y)\, dy,$$

$$(n = 1, 2, 3, \cdots \infty),$$

where x lies in the interval

$$(2) \qquad 0 \leqslant x \leqslant T,$$

and where the given functions f_n, g_n, h_n satisfy the following inequalities for all n, x, y, k, l :

$$(3) \qquad \sum_n |f_n(x)| = c, \quad |g_n(x, y)| \leqslant b, \quad \sum_n |h_n(k, l ; y)| \leqslant a,$$

a, b, c being absolute constants.

We replace the unknown functions $u_n(x)$ by the functions $w_n(x)$ according to the relations :

$$(4) \qquad w_n(x) = u_n(x) - f_n(x), \quad (n = 1, 2, \cdots).$$

The equations (1) then become for all $n \geqslant 1$:

$$(5) \quad w_n(x) = \int_0^x g_n(x, y) \sum_{k, l} h_n(k, l ; y) \{f_k(y) + w_k(y)\} \{f_l(y) + w_l(y)\}\, dy.$$

We shall solve this system by the method of successive approximations, and for this purpose we write :

$$w_n^{(0)}(x) = 0, \quad \text{and for } r \geqslant 1 :$$

$$(6) \quad w_n^{(r)}(x) =$$

$$\int_0^x g_n(x, y) \sum_{k, l} h_n(k, l ; y) [f_k(y) + w_k^{(r-1)}(y)] [f_l(y) + w^{(r-1)}(y)]\, dy.$$

We shall prove now that for all $r \geqslant 0$, the series $\sum_n |w_n^{(r)}(x)|$ lies under a fixed limit as soon as T is sufficiently small.

Let for all x in $0 \leqslant x \leqslant T$, and for all $r \geqslant 0$:

$$(7) \qquad v_r = \text{Max} \sum_n |w_n^{(r)}(x)|.$$

Then we get from (6) on account of (3) :

$$(8) \qquad v_r \leqslant ab\mathrm{T}(c + v_{r-1})^2.$$

Now we define an infinite sequence (A_r) as follows :

$$(9) \quad A_0 = 0, \quad A_r = 2\, ab\mathrm{T}\, (c^2 + A^2_{r-1}) \quad (r = 1, 2, \cdots).$$

On account of the inequality $2ab \leqslant a^2 + b^2$, we see that

$$(10) \qquad v_r \leqslant A_r \quad (r = 0, 1, 2, 3, \cdots).$$

We shall prove now that the sequence A_r is bounded. Take a fixed positive integer p, and let for all $r \leqslant p$:

$$A_r \leqslant 1, \ (r \leqslant p).$$

Then from (9) we have for all $r \leqslant p$:

$$A_{r+1} - A_r = 2ab'T\,(A_r^2 - A_{r-1}^2) = 2ab'T\,(A_r + A_{r-1})\,(A_r - A_{r-1}),$$

so that, since both A_r and A_{r-1} are supposed to be $\leqslant 1$,

$$|A_{r+1} - A_r| \leqslant 4ab'T\,|A_r - A_{r-1}|, \quad (r \leqslant p).$$

Therefore we find :

$$\begin{aligned} A_{p+1} &\leqslant |A_1| + |A_2 - A_1| + |A_3 - A_2| + \cdots + |A_{p+1} - A_p| \\ &\leqslant 2ab'Tc^2\{1 + 4ab'T + (4ab'T)^2 + \cdots + (4ab'T)^p\} \\ &< \frac{2ab'Tc^2}{1 - 4ab'T}, \end{aligned}$$

where it is assumed that $4ab'T < 1$.

Now, if we take T so that

$$T < \text{Min}\left(\frac{1}{8ab'}, \ \frac{1}{4abc^2}\right), \tag{11}$$

we get

$$A_{p+1} < 4ab'Tc^2 < 1.$$

We have, however, $A_1 = 2ab'Tc^2 < 1$; so that by induction we get for all $r \geqslant 1$:

$$A_r < 1 \quad (r = 1, 2, \cdots \infty). \tag{12}$$

From (7) and (10) we see therefore that the series $\sum_n |w_n^{(r)}(x)|$ is uniformly convergent and less than unity, provided x lies in the interval given by (11).

We go on to prove now that the doubly infinite series

$$\sum_n |w_n^{(1)}(x)| + \sum_r \sum_n |w_n^{(r+1)}(x) - w_n^{(r)}(x)| \tag{13}$$

is also uniformly convergent.

We have from (6)

$$\begin{aligned} w_n^{(r+1)}(x) - w_n^{(r)}(x) &= \int_0^x g_n(x, y) \sum_{k, l} h_n(k, l\,; y)\,\{[f_k(y) + w_k^{(r)}(y)]\,[f_l(y) + w_l^{(r)}(y)] - \\ &\qquad [f_k(y) + w_k^{(r-1)}(y)] \times [f_l(y) + w_l^{(r-1)}(y)]\}\,dy \\ &= \int_0^x g_n(x, y) \sum_{k, l} h_n(k, l\,; y)\,\{f_k(y)\,[w_l^{(r)}(y) - w_l^{(r-1)}(y)] + \\ &\qquad f_l(y)\,[w_k^{(r)}(y) - w_k^{(r-1)}(y)] + w_k^{(r)}(y)\,[w_l^{(r)}(y) - w_l^{(r-1)}(y)] \\ &\qquad + w_l^{(r-1)}(y)\,[w_k^{(r)}(y) - w_k^{(r-1)}(y)]\}\,dy. \end{aligned}$$

From (3) and (12) we get therefore for any x:

$$(14)\quad \sum_n |w_n^{(r+1)}(x) - w_n^{(r)}(x)| < ab\mathrm{T}(2c+2)\,\mathrm{Max}\sum_n |w_n^{(r)}(x) - w_n^{(r-1)}(x)|.$$

We see, therefore, that the series $\sum_n |w_n^{(r+1)}(x) - w_n^{(r)}(x)|$ converges uniformly provided the series $\sum_n |w_n^{(r)}(x) - w^{(r-1)}{}_n(x)|$ does so. We take T so small that it satisfies the inequality:

$$(15)\qquad \mathrm{T} \leqslant \frac{\gamma}{2ab\,(1+c)}, \quad \gamma < 1.$$

Then applying the reduction (14) r times, we get for x in (2):

$$(16)\quad \sum_n |w^{(r+1)}{}_n(x) - w_n^{(r)}(x)| < \{2ab\mathrm{T}(1+c)\}^r.\ \mathrm{Max}\sum_n |w^{(1)}{}_n(x) - w^{(0)}{}_n(x)| < \gamma^r.\ \mathrm{Max}\sum_n |w^{(1)}{}_n(x)|.$$

Summing both sides of (16) from $r=0$ to $r=\infty$, and remembering that $\mathrm{Max}\sum_n |w^{(1)}{}_n(x)| = v_1 \leqslant \mathrm{A}_1 < 1$, and that $\gamma < 1$, we see that the double series is uniformly convergent in $0 \leqslant x \leqslant \mathrm{T}$, where T is restricted by the relation (15).

It follows therefore that all the limiting values exist:

$$(17)\qquad \lim_{r\to\infty} w^{(r)}{}_n(x) = w_n(x) \quad (n = 1, 2, \cdots \infty),$$

and that for all x in $0 \leqslant x \leqslant \mathrm{T}$, the series $\sum_n |w_n(x)|$ is uniformly convergent.

Proceeding to the limit $r \to \infty$ in (6), we obtain that the function $w_n(x)$ satisfies the integral equation (5), and consequently $u_n(x) = w_n(x) + f_n(x)$ satisfies the integral equation (3).

We shall now establish the uniqueness of this solution.

Suppose that the system of integral equations (5) has another solution $\bar{w}_n(x)$ $(n = 1, 2, \cdots)$, such that the series $\sum_n |\bar{w}_n(x)|$ converges uniformly:

$$(18)\qquad \sum_n |\bar{w}_n(x)| = \bar{c}.$$

From the definitions of $\bar{w}_n(x)$ and $w_n^{(r+1)}(x)$, we get

$$\bar{w}_n(x) - w_n^{(r+1)}(x) = \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y) \{[f_k(y) + \bar{w}_k(y)]\,[f_l(y) + \bar{w}_l(y)] - [f_k(y) + w_k^{(r)}(y)]\,[f_l(y) + w_l^{(r)}(y)]\}\, dy$$

$$= \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y) \{f_k(y)\,[\bar{w}_l(y) - w_l^{(r)}(y)] + f_l(y)\,[\bar{w}_k(y) - w_k^{(r)}(y)] + w_k^{(r)}(y)\,[\bar{w}_l(y) - w_l^{(r)}(y)] + \bar{w}_l(y)\,[\bar{w}_k(y) - w_k^{(r)}(y)]\}\, dy.$$

From (3), (12) and (18) we obtain therefore :

$$(19)\quad \sum_n |\bar{w}_n(x) - w_n^{(r+1)}(x)| < abT(2c+1+\bar{c}).\ \mathrm{Max}\sum_n |\bar{w}_n(x) - w_n^{(r)}(x)|.$$

Now, we take T so small that besides (15) it satisfies also :

$$(20)\qquad T < \frac{q}{ab(2c+1+\bar{c})},\quad q < 1.$$

Then applying the reduction (19) $r+1$ times, we get

$$\sum_n |\bar{w}_n(x) - w_n^{(r+1)}(x)| < \{abT(2c+1+\bar{c})\}^r.\ \mathrm{Max}\sum_n |\bar{w}_n(x) - w_n^{(0)}(x)|$$

$$< q^r\ \mathrm{Max}\sum_n |\bar{w}_n(x)| = \bar{c}\ q^r.$$

Since $q < 1$, we get

$$\lim_{r\to\infty}\ \sum_n |\bar{w}_n(x) - w_n^{(r+1)}(x)| = 0,$$

which gives

$$\bar{w}_n(x) = \lim_{r\to\infty} w_n^{(r+1)}(x) = w_n(x),$$

$$(n = 1, 2, \cdots \infty).$$

This shows that the two solutions are really identical.

3. *Solution in the Unrestricted Domain.*

If the system

$$(1)\quad u_n(x) = f_n(x) + \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l\,; y) u_k(y) u_l(y)\ dy,\ (n = 1, 2, \cdots)$$

has to be solved for the unrestricted domian :

$$(2)\qquad 0 \leqslant x < \infty,$$

we must assume that the given functions satisfy :

$$(3)\qquad \sum_n |f_n(x)| = c,\quad \sum_n \left| \int_0^x g_n(x, y) h_n(k, l\,; y)\ dy \right| \leqslant a,$$

where c and a are constants independent of x, k, l.

We write for the successive approximations :

$$(4)\quad u_n^{(0)}(x) = f_n(x),\quad \text{and for } r \geqslant 1$$

$$(5)\quad u_n^{(r)}(x) = f_n(x) + \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l\,; y) u_k^{(r-1)}(y) u_l^{(r-1)}(y)\ dy.$$

We have now to show that these approximations converge to a unique limit. For this purpose we prove first that the series $\sum_n |u_n^{(r)}(x)|$ converges uniformly for all x and all r. Evidently, $\sum_n |u_n^{(r)}(x)|$ converges uniformly for all x provided $\sum_n |u_n^{(r-1)}(x)|$ does so, for we have :

$$(6)\qquad \sum_n |u_n^{(r)}(x)| \leqslant c + a\,[\mathrm{Max}\sum_n |u^{(r-1)}(x)|]^2.$$

From (3) and (4) we find $\sum_n |u_n^{(0)}(x)| = c$, so that

$$\sum |u_n^{(1)}(x)| \leqslant c + ac^2.$$

We assume now that

$$c < \frac{1}{4a}, \tag{7}$$

so that we find $\sum_n |u_n^{(1)}(x)| < 2c$ for all x. We substitute this in (6) and put $r = 2$, then we get

$$\sum_n |u_n^{(2)}(x)| < c + 4ac^2 < c + c = 2c,$$

and in general, for all $r \geqslant 1$, and all $x \geqslant 0$:

$$\sum_n |u_n^{(r)}(x)| < c + 4ac^2 < 2c. \tag{8}$$

We shall employ this inequality in proving further the uniform convergence of the double series

$$\sum_n |u_n^{(1)}(x) - u_n^{(0)}(x)| + \sum_r \sum_n |u_n^{(r+1)}(x) - u_n^{(r)}(x)|. \tag{9}$$

We have from (5)

$$u_n^{(r+1)}(x) - u_n^{(r)}(x) = \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l\,;\, y) \{u_k^{(r)}(y)u_l^{(r)}(y) - u_k^{(r-1)}(y)u_l^{(r-1)}(y)\}\, dy$$

$$= \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l\,;\, y) \{u_k^{(r)}(y)[u_l^{(r)}(y) - u_l^{(r-1)}(y)] + u_l^{(r-1)}(y)\,[u_k^{(r)}(y) - u_k^{(r-1)}(y)]\}\, dy.$$

From (3) and (8) we get therefore for all x:

$$\sum_n |u_n^{(r+1)}(x) - u_n^{(r)}(x)| < 4ac. \quad \operatorname{Max} \sum_n |u_n^{(r)}(x) - u_n^{(r-1)}(x)|.$$

Applying this reduction formula r times, we obtain:

$$\sum_n |u_n^{(r+1)}(x) - u_n^{(r)}(x)| < (4ac)^r. \quad \operatorname{Max} \sum_n |u_n^{(1)}(x) - u_n^{(0)}(x)|. \tag{10}$$

But

$$u_n^{(1)}(x) - u_n^{(0)}(x) = \int_0^x g_n(x, y) \sum_{k,l} h_n(k; l\,;\, y) u_k^{(0)}(y) u_l^{(0)}(y)\, dy,$$

so that for all $x \geqslant 0$, we have

$$\sum_n |u_n^{(1)}(x) - u_n^{(0)}(x)| \leqslant ac^2.$$

Moreover, since $4ac < 1$, we get $\sum_{r=0}^{\infty} (4ac)^r = \dfrac{1}{1 - 4ac}$. Thus, summing both sides of (10) from $r = 0$ to $r = \infty$, we see that the double series (9) converges uniformly for all x.

We deduce therefore that the limiting functions

$$\lim_{r\to\infty} u_n^{(r)}(x) = u_n(x) \quad (n = 1, 2, \cdots \infty) \tag{11}$$

exist and are continuous for all $x \geqslant 0$, and that the series $\sum_n |u_n(x)| = \lim_{r\to\infty} \sum_n |u_n^{(r)}(x)|$ is uniformly convergent. Proceeding now to the limit $r \to \infty$ in (5), we see that the function $u_n(x)$ found in (11) satisfies the integral equation (1), and is therefore the required solution.

To establish the uniqueness of this solution, we suppose that the integral equation (1) has another solution $\bar{u}_n(x)$ $(n = 1, 2, \cdots)$, which is such that the series $\sum_n |\bar{u}_n(x)|$ converges uniformly:

$$\sum_n |\bar{u}_n(x)| \leqslant 2c. \tag{12}$$

From the definitions of $\bar{u}_n(x)$ and $u_n^{(r+1)}(x)$ we get then

$$\begin{aligned}\bar{u}_n(x) - u_n^{(r+1)}(x) &= \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y) \{\bar{u}_k(y)\bar{u}_l(y) - u_k^{(r)}(y)u_l^{(r)}(y)\}\, dy \\ &= \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y) \{\bar{u}_k(y)\,[\bar{u}_l(y) - u_l^{(r)}(y)] \\ &\qquad + u_l^{(r)}(y)\,[\bar{u}_k(y) - u_k^{(r)}(y)]\}\, dy.\end{aligned}$$

On account of (3), (8) and (12) we get therefore for all x:

$$\sum_n |\bar{u}_n(x) - u_n^{(r+1)}(x)| < 4ac.\ \mathrm{Max} \sum_n |\bar{u}_n(x) - u_n^{(r)}(x)|;$$

and repeating this reduction $(r + 1)$ times:

$$\sum_n |\bar{u}_n(x) - u_n^{(r+1)}(x)| < (4ac)^{r+1}.\ \mathrm{Max} \sum_n |\bar{u}_n(x) - u_n^{(0)}(x)|. \tag{13}$$

Now, since

$$\bar{u}_n(x) - u_n^{(0)}(x) = \int_0^x g_n(x, y) \sum_{k,l} h_n(k, l; y)\bar{u}_k(y)\bar{u}_l(y)\, dy,$$

we have from (3) and (12) for all $x \geqslant 0$:

$$\sum_n |\bar{u}_n(x) - u_n^{(0)}(x)| \leqslant 4ac^2.$$

Thus, since $4ac < 1$, we obtain

$$\begin{aligned}\lim_{r\to\infty} \sum_n |\bar{u}_n(x) - u_n^{(r+1)}(x)| &< 4ac^2 \lim_{r\to\infty} (4ac)^r \\ &= 0,\end{aligned}$$

showing that for all $x \geqslant 0$:

$$\bar{u}_n(x) = \lim_{r\to\infty} u_n^{(r+1)}(x) = u_n(x) \quad (n = 1, 2, \cdots \infty). \tag{14}$$

The two solutions are therefore identical.

THE PHYSICAL IDENTITY OF ENANTIOMERS.

Part IV. The Raman Spectra of *Dextro* and *Laevo* Camphoric Acids and Camphoric Anhydrides.

By Bawa Kartar Singh
and
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Received July 8, 1937.

1. Introduction.

The recognition of the phenomenon of enantiomorphism in natural objects resulted in their division into two groups—symmetric and dissymmetric. The discovery of optical activity in certain organic substances in solution by Biot in 1815 led Pasteur as the result of his work on the tartaric acids in 1848 to propound his Law of Molecular Dissymmetry. According to this law, molecules of optically active substances, like all other geometrical figures, exhibit enantiomorphism, and the two optically active and opposite forms are related to one another as an object is to its non-superposable *exact* mirror image. The two forms are identical as regards the magnitude of their scalar and vectorial properties, though the direction of the vectorial properties, such as the rotation of the plane of polarisation of polarised light, etc., is opposite in the two cases. In the series of researches, which have been conducted to test this law, the magnitude of the rotatory power of the *d* and *l* forms of a compound has been shown to be identical.[1] The case of *d* and *l* camphoric acids cited by Campbell[2] as militating against this law was settled in Part I of this series.[3] It was shown that Campbell's results were based on impure substances and if sufficient care is taken to purify the substances, the rotatory power of the two forms is identical in magnitude. In a recent communication[4] by one of us, the identity of the enantiomers as regards the scalar properties, such as density, viscosity and refraction has been established. In the present paper, we propose to extend the application of Pasteur's principle to the Raman spectra of the optically active forms of camphoric acid and camphoric anhydride.

Special interest attaches to the study of Raman spectra of *d* and *l* camphoric acids. As already mentioned above, it was this pair of optically active acids, the alleged non-identity of whose physical properties was used

as an argument against the validity of Pasteur's principle. The two acids are also interesting, as they yield anhydrides which are optically inactive throughout the range of spectrum, λ 4358 to 6709. That this is not due to racemisation follows from the fact that the anhydrides yield, on hydrolysis, *d* and *l* camphoric acids, having $[\alpha]^{35°}_{Hg5461} = \pm 56°\cdot35$ in ethyl alcohol.[3] The phenomenal fall in rotatory power is attributed to the ring structure of the camphoric anhydrides. It is, therefore, of interest to compare the Raman spectra of the anhydrides with those of the acids to find out if there is any profound difference associated with the ring structure of the anhydrides.

2. *Experimental.*

The technique of complementary filters of R. Ananthakrishnan[5] for investigating crystals was employed. A circular pyrex mercury arc surrounded a double-walled experimental galss-tube which contained the crystals, the Raman spectrum of which was to be photographed. The outer jacket of the observation tube contained a moderately concentrated solution of iodine in carbon tetrachloride which filtered the incident radiation of the mercury arc spectrum and allowed only λ 4046 to pass through with sufficient intensity and served as the exciting line. The transversely scattered light was condensed by means of a lens on the slit of a Hilger two-prism glass spectrograph of high light-gathering power. Immediately in front of the slit of the spectrograph was placed a cell containing a solution of sodium nitrite of suitable concentration to absorb the exciting line from the scattered light before it entered the spectrograph. The Raman spectra were photographed on golden Iso-zenith plates, H and D, 1400, specially backed to prevent halation. The plates were measured by means of a Hilger cross-slide microscope. In the case of faint lines, however, the frequencies were determined only by visual estimation in comparison with an iron arc spectrum.

3. *Preparation and Purification of Materials.*

The *d* and *l* camphoric acids and the corresponding anhydrides were prepared and purified according to methods given in a previous communication,[3] and had the following constants :

	m.p.	$[\alpha]^{35°}_{Hg5461}$	
d-Camphoric acid ..	187°	+ 56°·35	5·25 per cent. solution in ethyl alcohol.
l-Camphoric acid ..	187°	− 56°·21	
d-Camphoric anhydride ..	221°	0·0	
l-Camphoric anhydride ..	221°	0·0	

The carefully purified substances gave a continuous background on the photographic plate. In order to overcome this difficulty, the substances were recrystallised from ethyl acetate, when the background became considerably clear.

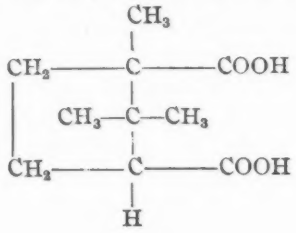
4. *Results.*

In Table I are given the wave-numbers of the Raman lines excited by λ 4046, the Raman shifts together with their relative intensities (visual), I and observed structural characters. The other symbols have the following meaning: s = sharp, b = broad and d = diffuse.

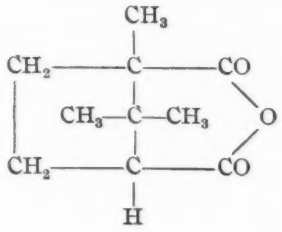
5. *Discussion of Results.*

The Raman spectra of *dextro* and *lævo* forms of both camphoric acid and camphoric anhydride are identical as regards the number, position and intensities of the lines. Pasteur's law, therefore, holds good in these cases, just as in the case of the optically active and opposite forms of camphor and borneol recently examined by one of us.[6]

The formulæ of camphoric acid (I) and its anhydride (II) are given below to correlate the chemical structure of the molecules with the Raman lines which they give on irradiation.



I



II

The crystals of camphoric acid and its anhydride have yielded eleven lines each. They are classified in Table II according to their modes of vibration.

The most intense lines in the whole spectrum are those due to the valence oscillations of the C–H group in the region 2743 to 2986.* The structure of this group of lines is strikingly different from that of other organic compounds. The lines at 2897, 2933, 2952 and 2986 are sharp and well-defined and superposed on a continuous background covering this region. The origin of this continuous spectrum is, however, not clear. The multiplicity of the C–H lines is to be attributed to the presence of three kinds of

* The figures given in this paper indicate wave-numbers per cm.$^{-1}$

TABLE I.
Exciting Line 4046·5 A.U. $\nu = 24705\ cm.^{-1}$

TABLE I.

Exciting Line 4046·5 A.U. $\nu = 24705\ cm.^{-1}$

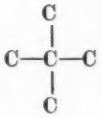
Time of exposure	48 hours			36 hours			48 hours			48 hours		
No.	*d*-Camphoric anhydride			*l*-Camphoric anhydride			*d*-Camphoric acid			*l*-Camphoric acid		
	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I
1	24098	607	6*s*	24098	607	6*s*	24101	604(?)	*ob*	24101	604(?)	*ob*
2	..	..	..	..	..	..	24000	705	3*s*	24000	705	3*s*
3	..	..	..	..	..	..	23968	737	1*d*	23967	738	0*d*
4	23539	1166	0	23539	1166	(*o*)	..	..	..	..	..	..
5	23465	1240	1	23468	1237	1	23468	1237	0	23468	1237	0
6	..	..	..	..	..	..	23429	1276	1	23429	1276	1
7	23391	1314	1	23392	1313	1	..	..	..	..	..	..
8	23276	1429	2*b*	23276	1429	2*b*	23276	1429	2*b*	23282	1423	2*b*
9	23220	1485	2*b*	23220	1485	2*b*	23249	1456	2*b*	23249	1456	2*b*
10	21962	2743	½	21962	2743	½	21962	2743	½	21962	2743	1*b*
11	21808	2897	6*b*	21806	2899	6*b*	21804	2901	3*b*	21811	2894	2*b*
12	21781	2924	4*b*	21779	2926	4*b*	21775	2930	4	21768	2937	3
13	21753	2952	4*b*	21753	2952	4*b*	..	..	..	..	..	..
14	21719	2986*	10*b*	21719	2986*	10*b*	21719	2186*	10	21719	2986*	8

* Indicates that the line has also been excited by 4077 A.U.

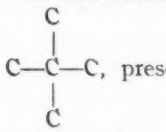
In the *d* and *l* camphoric acids, there is a continuous spectrum superposed on the lines at 2894, 2937 and 2985 cm.$^{-1}$

TABLE II.

Raman Frequencies in cm.$^{-1}$

No.	Camphoric acid	Camphoric anhydride	Classification
1	604 (*ob*)	607 (6*s*)	
2	705 (3*s*)	..	
3	737 (1*d*)	..	
4	..	1166 (*o*)	
5	1237 (*o*)	1240 (1)	C ⟷ C
6	1276 (1)	1314 (1)	
7	1429 (2*b*)	1429 (2*b*)	δ (C — H)
8	1456 (2*b*)	1485 (2*b*)	
9	2743 ($\frac{1}{2}$)	2743 ($\frac{1}{2}$)	
10	2897 (2*b*)	2897 (6*b*)	
11	2933 (3)	2925 (4)	C ⟷ H
12	..	2952 (4)	
13	2986 (10)	2986 (10)	

groups CH, CH_2 and CH_3, in these compounds. The deformation vibration of the CH_2 group is also split up into two frequencies at 1429 and 1485 in the anhydride and at 1429 and 1456 in the acid. The frequency shifts 1237 and 1276 in the acid and at 1166, 1240 and 1314 in the anhydride may be assigned either to the ring structure or to the C–C vibrations.

A striking feature of the Raman spectra of camphoric acids is the occurrence of a sharp and intense line at 705. It is shifted to about 607 in the camphoric anhydride. A similar line also occurs at 649 in the spectra of borneols and camphors.[6] This frequency shift is to be associated with molecules containing the quaternary carbon atom,  present in several terpenes and neopentane. It is interesting to recall the recent studies

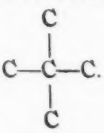
of Rank and Bordner[7] on the Raman spectra of a series of compounds, namely, tetramethyl methane, trimethyl pentenes, trimethyl pentane and tetramethyl pentane, whose molecules contain the above mentioned 'neopentyl' group. It was found that all these compounds give a Raman line of high intensity and extreme sharpness, the frequency varying from 726 to 765, depending on the compound. In silicon tetramethyl, this frequency is reduced to 598. It is thus clear that the symmetrical oscillations of the tetrahedral group, consisting of a carbon atom linked to four other carbon atoms (the so-called neopentyl group), which is present in several aliphatic hydrocarbons and terpenes, may be responsible for this sharp and intense Raman line. The frequency of this vibration is influenced by even small changes in the structure of the molecule ; but its characteristic sharpness and intensity remain the same.

The Raman lines below 600 could not be recorded by the experimental method adopted. The lines near 1700 region due to the carbonyl groups excited by λ 4046 of the mercury arc, fall in the region of λ 4358, and therefore, their presence could not be detected. The spectra are thus incomplete and a more detailed investigation of these compounds in the state of solution with particular reference to the polarisation characters of the lines would throw much light on the structure of these molecules.

6. *Summary.*

1. The Raman spectra of the *d* and *l* forms of camphoric anhydride and of camphoric acid in the crystalline state have been studied. The spectra of the two forms are identical, which, therefore, supports Pasteur's Law of Molecular Dissymmetry.

2. The lines due to the vibrations of the CH_2-groups are most intense in these compounds.

3. An intense sharp line at 706 cm.$^{-1}$ in camphoric acid is shifted to 607 cm.$^{-1}$ in its anhydride. These lines have been assigned to the symmetrical oscillations of the neopentyl group  .

4. The lines due to the (CH) vibrations are almost identical in the camphoric acid and its anhydride.

One of us (B. M.) is grateful to the Government of Orissa, for the grant of a Research Scholarship which enabled him to take part in the early stages of this work. Our thanks are due to Sir C. V. Raman for affording

necessary laboratory facilities and for his interest in this work. We also wish to thank Dr. C. S. Venkateswaran and Mr. R. Ananthakrishnan for valuable assistance.

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A NEW EVALUATION OF THE NUMBER $\Gamma(k)$ IN WARING'S PROBLEM.

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(Communicated by Dr. S. Chowla.)

1. After Hardy and Littlewood the number $\Gamma(k)$ is defined as the least s such that every arithmetical progression contains infinitely many numbers of the form $x_1^k + \cdots + x_s^k$, where the x's are integers $\geqslant 0$. In this paper it is shown that

Theorem I. *If* p *is an odd prime and if* $(2\mathrm{p} + 1)$ *is not a prime, then*

$$\Gamma(p) \leqslant 2\left[\frac{p}{3}\right] + 2$$

where [x] *denotes the greatest integer contained in* x.

This is an improvement on Hardy and Littlewood's result* that $\Gamma(p) \leqslant p$ for $p > 3$, which is the best inequality to date. Since there are infinitely many primes p for which $2p + 1$ is composite, our theorem shows conclusively the new result that $\Gamma(k) < k$ for infinitely many integers k.

We note the following complement to Theorem I :

Theorem 2. *If* p *is a prime greater than* 3 *and* $2\mathrm{p} + 1$ *is also a prime, then* $\Gamma(\mathrm{p}) = \mathrm{p}$.

This follows trivially from Hardy and Littlewood's result $\Gamma(p) \leqslant p$ in view of the fact that $0, +1, -1$ are the only pth power residues (mod q) where $q = 2p + 1$.

The method of proof is new and rests mainly on simple arithmetical considerations.

2. $\Gamma(k, q^\theta)$ is conveniently defined as the least s such that every residue class (mod q^θ) is representable as $x_1^k + \cdots + x_s^k$ where the x's are integers. In what follows p and q will denote odd primes, and θ denotes an integer $\geqslant 1$.

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* "Partitio numerorum (VIII)," *Proc. Lond. Math. Soc.*, 1928, **27**, 518–542.

3. *Proof of Theorem* I: The following lemmas are used:

Lemma 1.† *Let* $\alpha_1, \cdots, \alpha_m$ *be* m *different residue classes* (mod q); *let* $\beta_1, \cdots, \beta_n$ *be* n *different residue classes* (mod q); *let* $\gamma_1, \cdots, \gamma_l$ *be all those different residue classes representable as*

$$\alpha_i + \beta_j \qquad (1 \leqslant i \leqslant m, \quad 1 \leqslant j \leqslant n)$$

Then $l \geqslant m + n - 1$ *if* $m + n - 1 \leqslant q$, *and otherwise* $l = q$

Lemma 2. *If* $x_1^p + \cdots + x_s^p \equiv n \pmod{p^2}$ *is soluble with at least one of the* x's *prime to* p, *then so is*

$$x_1^p + \cdots + x_s^p \equiv n \pmod{p^\theta}$$

where $\theta \geqslant 3$, *soluble with at least one of the* x's *prime to* p.

Proof. Without loss of generality let $(x_1, p) = 1$. If

$$x_1^p + \cdots + x_s^p \equiv n \pmod{p^{\theta-1}} \qquad [\theta \geqslant 3]$$

write

$$x_1^p + \cdots + x_s^p = n + mp^{\theta-1}.$$

Hence

$$(x_1 + m_1 p^{\theta-2})^p + x_2^p + \cdots + x_s^p$$
$$= n + p^{\theta-1}(m + m_1 x_1^{p-1}) + \mathrm{M}(p^\theta)$$

where M (x) denotes a multiple of x. Since $(x_1, p) = 1$ we can choose m_1 so that $m + m_1 x_1^{p-1} \equiv 0 \pmod{p}$ and the lemma follows.

Lemma 3. *We can find an integer* u *such that*

$$(x+1)^p - x^p - 1 = pu, \qquad p \nmid u.$$

Proof.

$$\frac{(x+1)^p - x^p - 1}{p} \equiv 0 \pmod{p}$$

is equivalent to, when $1 \leqslant x \leqslant p - 1$,

$$\frac{p-1}{2} x^{p-2} + \cdots + x + 1 \equiv 0 \pmod{p} \tag{1}$$

since by Fermat's theorem $x^{p-2} \equiv 1 \pmod{p}$. Since the congruence (1) has at most $(p-2)$ incongruent roots (mod p), the lemma follows.

Lemma 4. $np \equiv x^p + y^p + z^p \pmod{p^2}$
is soluble with x *prime to* p *for any given value of* n.

Proof. If $n \equiv 0 \pmod{p}$ the lemma is obviously true. If $(p, n) = 1$ choose v so that $uv \equiv n \pmod{p}$, where u is found in lemma 3. Then

$$np \equiv (up)\, v \pmod{p^2}$$
$$\equiv up \cdot v^p \pmod{p^2}$$

From this and lemma 3, lemma 4 follows since (from lemma 3),

$$up = x^p + y^p + z^p.$$

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† *Journ. Lond. Math. Soc.*, 1935, **10**, 30-32. I have previously used this lemma due to Davenport to show that $\Gamma(k) \leqslant 4k$.

Lemma 5. $m \equiv x_1^p + x_2^p + x_3^p + x_4^p \pmod{p^2}$
is soluble with $(x_1, p) = 1$ *for any* m.

Proof. $m = m^p + np$, and lemma 4.

Lemma 6. $\Gamma(p, p^\theta) \leqslant 4$ for $\theta \geqslant 1$.

Proof. *Since* $x^p \equiv x \pmod{p}$, we have

$$\Gamma(p, p) = 1.$$

Further, from lemmas 2 and 5,

$$\Gamma(p, p^\theta) \leqslant 4 \quad \text{for } \theta \geqslant 2.$$

Hence lemma 6 is proved.

Lemma 7. *If* $q \nmid k$, $q \nmid R$ *the solubility of* $x^k \equiv R \pmod{q^\theta}$ *implies the solubility of* $x^k \equiv R \pmod{q^{\theta+1}}$ *where* $\theta \geqslant 1$.

Proof. If $x^k = R + mq^\theta$ then

$$(x + m_1 q^\theta)^k = R + q^\theta (m + k m_1 x^{k-1}) + M(q^{\theta+1}).$$

Since R is prime to q, we have $(x, q) = 1$, and hence m_1 can be chosen so that

$$m + k m_1 x^{k-1} \equiv 0 \pmod{q}.$$

Hence the lemma.

Lemma 8. *If* $q \not\equiv 1 \pmod{p}$, $q > 2$, *the congruence* $x^p + y^p \equiv n \pmod{q}$ *is soluble for every* n *with* $xy \not\equiv 0 \pmod{q}$.

Proof. If g is a primitive root of q, the numbers $g^p, g^{2p}, \cdots, g^{(q-1)p}$ are congruent in some order to $1, 2, 3, \cdots, (q-1)$.

The lemma follows immediately.

Lemma 9. $\Gamma(p, q^\theta) \leqslant 2$ if $q \not\equiv 1 \pmod{p}$, $q > 2$, $q \neq p$, $\theta \geqslant 1$.

Proof. Lemmas 7 and 8.

Lemma 10. $x^p \equiv n \pmod{2^\theta}$ *is soluble if* n *is odd and* $\theta \geqslant 1$.

Proof. Obvious for $\theta = 1$. Then apply lemma 7.

Lemma 11. $\Gamma(p, 2^\theta) \leqslant 2$.

Proof. $(2m + 2) = (2m + 1) + 1 \equiv x^p + 1 \pmod{2^\theta}$ by lemma 10. Hence the lemma.

Lemma 12. *If* α *and* β *are* kth *power residue* (mod q) *then so are* $\alpha\beta$ *and* $\frac{\alpha}{\beta}$ *where* $\frac{\alpha}{\beta}$ *denotes the integer* γ *such that* $\beta\gamma \equiv \alpha \pmod{q}$ [*provided* $\beta \neq 0$].

Proof. $\alpha \equiv x^k$, $\beta \equiv y^k$.

Hence $\alpha\beta \equiv (xy)^k$ and $\frac{\alpha}{\beta} \equiv \frac{x^k}{y^k} \equiv (xz)^k$ where z is chosen so that

$$yz \equiv 1 \pmod{q}.$$

Lemma 13. *Let* $q = sp + 1$, $s \geqslant 4$; *and let* $a_0, a_1, a_2, \cdots, a_s$ *be all the positive reduced incongruent* pth *power residues* (mod q), *arranged in ascending*

order of magnitude so that $a_0 = 0$. *Let* $\gamma_1, \cdots, \gamma_l$ *be all those different residue classes representable as*

$$a_i + a_j \; [0 \leqslant i, j \leqslant s].$$

Then $l \geqslant 3s + 1$. *In other words, the number of incongruent numbers of the form* $x^p + y^p \pmod q$ *is at least* $3s + 1$ *when* $q = sp + 1$, $s \geqslant 4$.

Proof. It is evident that $a_1 = 1$ and that $-a_j$ is always a residue for $0 \leqslant j \leqslant s$, since p is odd. In the proof of this fundamental lemma, R will denote a number which is congruent to a pth power residue (mod q), N will denote a number which is not an R. We consider now the cases which arise for different values of a_2,

(A) $a_2 > 4$ (Hence 2, 3 and 4 are N's)

(B) $a_2 = 4$ (hence 2 and 3 are N's)

(C) $a_2 = 3$ (hence 2 is an N)

(D) $a_2 = 2$.

These are all the possible cases. We first consider

CASE (A). $a_2 > 4$. The numbers

$$0, a_1, \cdots, a_s, \quad 2a_1, \cdots, 2a_s$$

are mutually incongruent by lemma 12 since 2 is an N. Further these $(2s + 1)$ numbers are γ's. Our lemma is proved in case (A) if we can find a number W such that

(2) W is a γ, W and $\frac{W}{2}$ are N's, for then the $(3s + 1)$ numbers

$$0, a_1, \cdots, a_s, 2a_1, \cdots, 2a_s, Wa_1, \cdots, Wa_s$$

are γ's which are mutually incongruent by (2) and lemma 12.

Consider the sub-cases :

(i) a_2 odd ; then $W = a_2 - 1$ satisfies (2).

(ii) a_2 even, $a_2 + 1$ is an R ; here, if $a_2 + 2$ is an N, we choose $W = a_2 + 2$ for this satisfies (2). But if $a_2 + 2$ is an R we put $W = a_2^2 - a_2 - 2 = (a_2 - 2)(a_2 + 1)$.

For obviously W is not an R by lemma 12, and for the same reason since

$$\frac{W}{2} = (a_2 + 1)\frac{a_2 - 2}{2}$$

it is clear that $\frac{W}{2}$ is not an R. W is a γ since a_2^2 is an R and $-a_2 - 2$ is an R. Note that the argument breaks down if $a_2 \equiv -1$, *i.e.*, when $s = 2$.

(iii) a_2 even, $a_2 + 1$ is an N ; If $a_2 + 1$ or $a_2 - 1$ is twice an N, our lemma is proved as before. Let therefore each of the numbers $a_2 + 1$ and $a_2 - 1$ be twice an R. If $2a_2 - 2$ is an R then we can take $W = 2a_2 - 2 - a_2$

for this W satisfies (2). Let therefore $2a_2 - 2$ be an N. Then $W = a_2^2 - 1$ is obviously a γ and W is not an R for $a_2^2 - 1 = \frac{a_2 + 1}{2} \cdot (2a_2 - 2)$; further W is not twice an R for

$$\frac{a_2^2 - 1}{2} = \frac{a_2 + 1}{2} \cdot (a_2 - 1).$$

[As in case (ii) above we remark that the only exception arises when $a_2 = -1$ (which means $s = 2$) or $a_2 = 1$ (which is impossible) for in these cases $W = 0$ which is an R.]

CASE (B). $a_2 = 4$.

Assume that the lemma is false in this case. If 3 is twice an N, the lemma would be true for then $W = 3$ would satisfy (2). Hence let 3 be twice an R, whence 3^2 is an R; now $5 (= 4 + 1)$ is a γ and hence either 5 is an R or twice an R, as otherwise the lemma would be true. Hence 5^2 is an R. Thus $1^2, 2^2, 3^2, 4^2, 5^2$ are all R's.

Let $1^2, 2^2, \cdots, (2n-1)^2$ be R's. Then $(2n)^2 = 2^2 \cdot n^2$ is obviously an R; further, $2n + 1 = (n+1)^2 - n^2$ is a γ. Hence if $2n + 1$ is an R or if $\frac{2n+1}{2}$ is an R, then $(2n+1)^2$ is an R, and if neither case holds the lemma would be true. Hence $(2n+1)^2$ is an R. Thus by induction every quadratic residue is an R. The number of quadratic residues (mod q) being $\frac{q-1}{2}$ we have $\frac{q-1}{2} \leqslant s$, *i.e.*, $q \leqslant 2s + 1$, *i.e.*, $p \leqslant 2$, which is contrary to hypothesis. And hence our lemma is proved for $a_2 = 4$, since the assumption that it is false leads to a contradiction.

CASE (C). $a_2 = 3$.

If 4 is an N then the lemma is proved for $W = 4$ satisfies (2). If 4 is an R the proof proceeds as in case (B).

CASE (D). $a_2 = 2$. Consider the sub-cases

(i) 3 is an N, 9 is an N; the $(3s + 1)$ numbers $0, a_1, \cdots, a_s, 3a_1, \cdots, 3a_s, 9a_1, \cdots, 9a_s$ are γ's since $3 = 2 + 1$ and $9 = 2^3 + 1$, and are mutually incongruent by lemma 12. Thus the lemma would follow.

(ii) 3 is an N, 9 is an R. Assume that the lemma is false. If 5 is an N and $\frac{5}{3}$ is an N, the $(3s + 1)$ numbers

$$0, a_1, \cdots, a_s, 3a_1, \cdots, 3a_s, 5a_1, \cdots, 5a_s$$

are γ's because $3 = 2 + 1$, $5 = 2^2 + 1$ and are mutually incongruent by lemma 12.

Hence 5 is an R or $\frac{5}{3}$ is an R and so in either case 5^2 is an R. Thus $1^2, 2^2, 3^2, 4^2, 5^2$ are R's. Proceeding as in case (B) the lemma is easily proved for we arrive at the contradiction that every quadratic residue of q is an R.

(iii) Let 3 be an R ; then 1, 2, 3, 4 are R's. Let $(\beta+1)$ be the first N occurring amongst the positive integers less than q. Then $1, 2, 3, \cdots, \beta$ are all R's. And $\beta+1$ is odd for if $2/(\beta+1)$ then $\beta+1=2$. $\frac{\beta+1}{2}$ would be an R since 2 and $\frac{\beta+1}{2}$ are R's. Hence $2/(\beta+2)$ whence $\beta+2=2$. $\frac{\beta+2}{2}$ is an R. Now it is easily seen that $(\beta+1)^2$ is a γ, for $(\beta+1)^2 = \beta(\beta+2)+1$ and $\beta(\beta+2)$ is an R. Let $(\beta+1)^2$ be an N, then the $(3s+1)$ numbers

$$0, a_1, \cdots, a_s, (\beta+1)a_1, \cdots, (\beta+1)a_s,$$
$$(\beta+1)^2 a_1, \cdots, (\beta+1)^2 a_s.$$

are mutually incongruent γ's by lemma 12.

If, however, $(\beta+1)^2$ is an R, then the numbers $1^2, 2^2, \cdots, (\beta+2)^2$ are all R's. Assuming the lemma is false we will show that $(\beta+3)^2$ is an R. For if $(\beta+3)$ is an R, $(\beta+3)^2$ is in any case an R. If $(\beta+3)$ is not an R, then $\frac{(\beta+3)}{(\beta+1)}$ must be an R. For otherwise the lemma would be true. To prove this statement consider the numbers

$$0, a_m, (\beta+1)a_m, (\beta+3)a_m \quad [1 \leqslant m \leqslant s].$$

These $(3s+1)$ numbers are mutually incongruent, and are γ's if we show that $(\beta+3)$ is a γ. Put $\beta+3 = 2^m t$ where t is odd and $\leqslant \beta+3$. But all odd numbers upto $2\beta+3$ are γ's, *e.g.*, $2\beta+3 = (\beta+2)^2 - (\beta+1)^2$. Since 2^m is an R, $\beta+3$ is a γ. Hence $\frac{(\beta+3)^2}{(\beta+1)^2}$ is an R, whence $(\beta+3)^2$ is an R. Proceeding in this way and assuming that the lemma is false at each stage we find that all the quadratic residues of q are R's, which gives a contradiction as before.

Thus the lemma is proved in all cases : (A), (B), (C) and (D).

Lemma 14. *Let* $q = sp+1$, $s \geqslant 4$.

Then

$$\Gamma(p, q) \leqslant 2\left[\frac{p}{3}\right] + 2.$$

Proof. By lemma 13 the number of incongruent numbers of the form $x_1^p + x_2^p \pmod q$ is at least $3s+1$. By lemma 1 it follows that the number of incongruent numbers of the form $x_1^p + x_2^p + x_3^p + x_4^p \pmod q$ is at least $2(3s+1)-1$ or q, whichever is the smaller. Hence, by another application of lemma 1, the number of incongruent numbers of the form $x_1^p + \cdots + x_6^p \pmod q$ is Min $(9s+1, q)$. Proceeding thus, the number

of incongruent numbers of the form $x_1^p + \cdots + x_t^p \pmod q$ is

$$\text{Min } \{(3t\ s + 1),\ q)\}$$

But $3ts + 1 \geqslant q$ if $3ts \geqslant sp$

i.e., if $t = \left[\frac{p}{3}\right] + 1$. Hence,

$$\Gamma(p, q) \leqslant 2t = 2\left[\frac{p}{3}\right] + 2.$$

Lemma 15. $\Gamma(p, q^\theta) \leqslant 2\left[\frac{p}{3}\right] + 2$

where $q = sp + 1$, $s \geqslant 4$, $\theta \geqslant 1$.

Proof. Lemmas 7 and 14.

4. *Concluding Argument.*

By lemma 11, $\Gamma(p, 2^\theta) \leqslant 2$ for $\theta \geqslant 1$

By lemma 6, $\Gamma(p, p^\theta) \leqslant 4$ for $\theta \geqslant 1$

By lemma 9, $\Gamma(p, q^\theta) \leqslant 2$ for $q \neq p$, $q \not\equiv 1 \pmod p$, $q > 2$, $\theta \geqslant 1$.

By lemma 15, $\Gamma(p, q^\theta) \leqslant 2\left[\frac{p}{3}\right] + 2$

where $q = sp + 1$, $s \geqslant 4$, $\theta \geqslant 1$.

Since $2p + 1$ is not a prime, we have $s \geqslant 4$. Hence,

$$\Gamma(p) = \max_q \Gamma(p, q^\theta) \leqslant 2\left[\frac{p}{3}\right] + 2,$$

which is Theorem I.

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